

***United States Court of Appeals
for the
District of Columbia Circuit***



**TRANSCRIPT OF
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APPENDIX TO APPELLANT'S BRIEF

IN THE
United States Court of Appeals
FOR THE DISTRICT OF COLUMBIA

55

Appeal No. 8406

EASTMAN KODAK COMPANY,

Appellant,

vs.

CONWAY P. COE, Commissioner of Patents,

Appellee.

**APPEAL FROM THE JUDGMENT OF THE
DISTRICT COURT OF THE UNITED STATES
FOR THE DISTRICT OF COLUMBIA**

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APPENDIX.

Complaint for Issuance of United States
Letters Patent.

IN THE DISTRICT COURT OF THE UNITED STATES

1

FOR THE DISTRICT OF COLUMBIA

CIVIL ACTION No. 11,596

EASTMAN KODAK COMPANY
343 State Street, Rochester, New York

Plaintiff

vs.

CONWAY P. COE, Commissioner of Patents,
Washington, D. C.

Defendant

I. The jurisdiction of this Court depends upon the Patent Laws of the United States, this complaint being filed under Section 4915, Revised Statutes (Compiled Statutes 9460; U. S. Code Title 35, Section 63), as amended by Act of March 2, 1927 and Act of August 5, 1939.

II. The plaintiff, EASTMAN KODAK COMPANY, is by an assignment in writing executed on the 7th day of March, 1939, and recorded in the United States Patent Office on March 29, 1939, in Liber S-178, Page 612, of the Transfer of Patents, the sole owner of the entire right, title and interest in and to an application for United States Letters Patent of KARL SCHINZEL, for improvements in PHENOLIC AND NAPHTHOLIC COUPLERS CONTAINING SULFONAMIDE GROUPS, filed in the United States Patent Office on March 24, 1939, Serial No. 263,945, a continuation-in-part of application Serial No. 151,811,

filed July 3, 1937, and the improvements disclosed and claimed therein.

III. The Board of Appeals of the United States Patent Office has refused to allow six claims of said KARL SCHINZEL application, Serial No. 263,945, which claims are as follows:

7. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

8. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

9. A photographic image comprising a dye formed by the coupling of the development product of a para-phenylenediamine developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

10. A photographic image comprising a dye formed by the coupling of the development product of a para-phenylenediamine developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

11. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-8-sulfonamide.

12. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-3:6-disulfonamide.

IV. The defendant, CONWAY P. COE, Commissioner of Patents of the United States, by the aforesaid decision of the Board of Appeals of the United States Patent Office has refused and still refuses to grant Letters Patent of the United States to the Plaintiff, EASTMAN KODAK COMPANY, an assignee of said KARL SCHINZEL, on said six claims recited in Paragraph III hereof, of said application Serial No. 263,945.

V. The said decision of the Board of Appeals was rendered on or about the 3rd day of December, 1940, and within six months last past, and no appeal has been taken from said decision of the Board of Appeals to the Court of Customs and Patent Appeals, and no such appeal is pending, or has been decided.

WHEREFORE, the Plaintiff, EASTMAN KODAK COMPANY, demands that this Honorable Court authorize the Commissioner of Patents to issue to Plaintiff, EASTMAN KODAK COMPANY, Letters Patent of the United States embodying said claims 7, 8, 9, 10, 11, and 12, upon the filing in the United States Patent Office of a certified copy of such adjudication, and upon compliance with the requirements of the law for such cases made and provided.

EASTMAN KODAK COMPANY,

By CLARENCE M. FISHER,
Attorney for Plaintiff,
National Press Building,
Washington, D. C.

NEWTON M. PERRINS,
R. FRANK SMITH,
343 State Street,
Rochester, New York.
Of Counsel.

Answer to the Complaint.

To the Honorable the Justices of the District Court of the United States for the District of Columbia.

I, II, III. Defendant admits the allegations of paragraphs I, II, and III.

IV. He admits that by a decision rendered by the Board of Appeals on December 3, 1940, he has refused and still refuses to issue to plaintiff a patent containing any one of claims 7 to 12, inclusive, of the application of Karl Schinzel, Serial No. 263,945, filed in the Patent Office on March 24, 1939, and entitled "Phenolic and Naphtholic Couplers Containing Sulfonamide Groups", which claims are as set out in paragraph III. He denies that his refusal is wrongful or that plaintiff is lawfully entitled to receive a patent including any of said claims as it is deemed that the said claims are unpatentable in view of the following prior patent and for the reasons given in the statement of the examiner in answer to the appeal and the decision of the Board of Appeals, copies of which will be furnished at the trial:

Fischer, 1,102,028, June 30, 1914.

Profert of a copy of this patent is hereby made.

V. He admits the allegations of paragraph V.

W. W. COCHRAN, Solicitor,
United States Patent Office,
Washington, D. C.

Attorney for Defendant.

June 10, 1941.

I hereby certify that a copy of this ANSWER TO THE COMPLAINT was mailed today, June 10, 1941, to the attorney for plaintiff, Clarence M. Fisher, 834 National Press Building, Washington, D. C.

W. W. COCHRAN,
Solicitor.

FINDINGS OF FACT

1. This is an action under Section 4915 of the Revised Statutes (U. S. C. title 35, sec. 63) in which it was sought to have the Court find that the plaintiff, Eastman Kodak Company, as assignee of the application of Karl Schinzel, Serial No. 263,945, is entitled to have issued to it a patent containing claims 7 to 12, inclusive, of the said application.

2. The Schinzel application relates to color photography and discloses a method of producing colored images by developing an exposed silver halide emulsion with a primary aromatic amino developing agent in the presence of a coupler compound comprising a naphthol or phenol containing a sulfonamide group.

3. Claims have been allowed in the Schinzel application to a developer comprising an aromatic amino developing agent and the particular coupler compound disclosed, and claims have also been allowed to the method of producing images by the use of this developer and a silver halide emulsion. The claims involved in the present action are drawn to an image comprising a dye formed by the use of the same coupler and developing agent which are recited in the allowed claims.

4. The patent to Fischer, No. 1,102,028, discloses a product which differs from that of the Schinzel application only in the specific coupler compound used.

5. The only novel element of the claims here involved is the coupler compound, which compound is used in exactly the same manner as the corresponding coupler compound of the Fischer patent.

6. The claims here involved are drawn to an old combination of a coupler compound and a developing agent to form a photographic image, and are, therefore, unpatentable.

7. The claims here involved are unpatentable over the Fischer patent.

7

CONCLUSIONS OF LAW

1. The plaintiff is not entitled to a patent containing any of claims 7 to 12 of the Schinzel application, No. 263,945.

2. The Bill of Complaint should be dismissed as to all the claims involved.

8

Judgment.

This cause having come on to be heard and having been tried in open court and argued by counsel for the respective parties upon the pleadings and proofs adduced and submitted to the Court,

It is ADJUDGED this 27th day of October, 1942, that the complaint in this case be, and the same hereby is dismissed with costs against the plaintiff.

MATTHEW F. McGUIRE,
Justice.

Approved as to Form:

CLARENCE M. FISHER,
Attorney for Plaintiff.

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Evidence on Behalf of the Plaintiff

PAUL WENDELL VITTUM was called as a witness for and on behalf of the plaintiff and, having been first duly sworn, was examined and testified as follows:

Direct Examination by Mr. Smith:

Q. State your name, age, and residence. A. Paul Wendell Vittum, age 33, residence Rochester, New York.

Q. What is your occupation? A. I am a research chemist.

Q. By whom are you employed? A. Eastman Kodak Company, Rochester, New York.

Q. How long have you been employed by them? A. For nine years.

Q. And what has been your work during that time? A. The first two years I was employed in the photographic chemistry division of the research laboratories, doing research work on general problems of photographic chemistry, and the remaining time I have been employed in the color laboratories doing research work on color photographic processes, and predominantly those processes employing color-forming developers.

Q. What are your educational qualifications as a chemist? A. I received an A. B. degree in chemistry from Cornell College, Mount Vernon, Iowa, and a Ph.D. degree in organic chemistry from Cornell University, New York.

Q. During your employment by Eastman Kodak Company have you tested any couplers or color formers? A. Yes, I have. 19

Q. About how many would you say you have tested? A. Oh, as an estimate, I should say in the neighborhood of two thousand.

Q. Are you familiar with the Schinzel application 263,945? A. Yes, I have read the application.

Q. What is the process that it describes? A. The Schinzel application refers to a group of color formers for producing dye images of a cyan or a blue-green color characterized by the fact that the couplers contain a grouping of the sulfonamide type.

Q. What are those couplers used for? A. Those couplers are used for the production of cyan dye images, mainly in the production of natural three-color photographs—natural-color photographs—in combination with other dyes produced in the same film.

Q. What do you mean by cyan? What color is that? A. A cyan is a term used to describe a color which you might call blue-green. That is, a cyan dye absorbs light from the red portion of the spectrum.

* * * *

- 20 Mr. Smith: I offer in evidence as Exhibit 1 a copy of the Schinzel application, Serial No. 263,945, about which the witness has testified.

(Certified copy of Schinzel application No. 263,945 was marked Plaintiff's Exhibit No. 1 and received in evidence.)

Q. Are you familiar with the Fischer patent 1,102,028, which was cited by the Patent Office in this Schinzel application? A. Yes, I am.

Q. What does it disclose with reference to cyan couplers? A. It discloses phenols and naphthols as cyan couplers and mentions certain substitution products of those compounds, including sulfonic acid derivatives.

* * * *

- 21 Q. Will you refer to this sheet, Exhibit 2, and explain a little more in detail the distinction between the couplers disclosed in the Schinzel application and the couplers disclosed in the Fischer patent? A. The couplers mentioned by Fischer are not defined exactly. As I recall, the exact wording of the Fischer specification says, "naphthol sulfonic acid," which could refer to a variety of arrangements of the groups within the molecule. For example, you have on this sheet the two compounds which would fall under the Fischer definition: "1-naphthol-4-sulfonic acid" and "1-naphthol-5-sulfonic acid." Both of those couplers are characterized by the presence in the molecule of the sulfonic acid, but that is the SO_2OH grouping. The Schinzel couplers, on the other hand, are characterized by the presence in the molecule of the substituent group SO_2NH , which is commonly referred to as a sulfonamide linkage.

Q. Would these couplers be expected to produce the same color dye when reacted with the oxidation product of an aromatic amino developing agent? A. Yes, I think that so far as the color of the dye is concerned that is largely determined by the naphthol nucleus itself. Alpha naphthol is known to yield a blue or blue-green dye, and the presence of the sulfonic acid

group or of the sulfonamide group might modify that color to a certain degree, but it would still fall within the range of blue-green or cyan dyes.

Q. Did you ever actually compare any dyes of the Schinzel application with dyes made from naphthol sulfonic acid? A. Yes, I did. I made a comparison among the five of the specific couplers described in the Schinzel application with four compounds selected to represent typical sulfonic acid derivatives of alpha naphthol which would correspond to the Fischer type.

* * * *

Q. What were the results of those tests, briefly? A. We 22
found in those tests that of the sulfonic acid derivatives of alpha naphthol—that is, of the Fischer couplers—only one yielded a dye image at all. The others gave no dye image or no appreciable dye image. The Schinzel couplers, on the other hand, all yielded dye images appearing to have useful characteristics. By the Court:

Q. You mean they were all more or less permanent and would not wash out; is that it? A. Yes; the main difference between the two groups of couplers was that the Fischer couplers, except for the one, gave dyes which bled out of the gelatin, and we got no dye image remaining. The Schinzel couplers, on the other hand, all gave good dye images.

* * * *

Mr. Smith: And as Plaintiff's Exhibit 3-B, I offer the accompanying sheet of dye strips.

(Sheet of dye strips was marked Plaintiff's Exhibit No. 3-B, and received in 23
evidence.)

By Mr. Smith:

Q. On those dye strips, which is the example of Fischer which gave a dye image? A. Strip No. 8.

Q. And which ones are of the Schinzel type? A. Nos. 2 to 7 are dyes of the Schinzel type.

Q. What type film was used in those tests? A. The film that was used in those tests was the regular cinepositive motion picture film.

Q. What was done after formation of the silver and dye image? A. After formation of the silver and dye image—that is, that formed during the color-development step—the strips are washed and then fixed to remove the residual silver halide; and following that the strips were subjected to an oxidizing bath to remove the silver formed during development, and one normally uses for that purpose a solution of potassium ferricyanide.

Q. So that the resulting strips contain only a dye image, if any, so formed; is that right? A. Yes.

* * * *

- 24 Q. What tests did you then make? A. The tests made at this time were similar to those begun before but more extended. Up to this time we had had available samples of only a few of the Schinzel couplers, and we asked Dr. Weissberger of the synthetic organic research laboratory to prepare for us samples of all the Schinzel couplers, and we obtained some further samples of representative compounds of the Fischer type. These were then carefully compared by producing dye images of large enough area so that one could obtain spectrophotometric curves from which we hoped to obtain a careful comparison of the color characteristics of the Schinzel couplers as compared with the one Fischer dye which we were able to produce.

* * * *

- 25 Q. Do you have the dye strips that you obtained in those tests? A. Yes, I have the strips here.

Mr. Smith: I offer in evidence as Exhibit 6-A the dye strips about which the witness has testified.

(Dye strips were marked Plaintiff's Exhibit No. 6-A and received in evidence.)

Q. What was done with these dye strips? A. These dye strips were prepared in such a manner as to obtain, as closely as possible, equal dye densities from the various couplers. The strips were then submitted to the physics department of the research laboratory, who obtained spectrophotometric curves from the dye images, using their automatic recording spectrophotometer.

Q. And did you obtain curves from these dyes? A. Yes.
By the Court:

Q. These curves are supposed to represent the intensity of the color in the dye; is that it? A. The intensity is represented by the height of the maximum curve. The most useful function of such curves is that they represent a definition of the color itself. That is, they show what region of the spectrum is absorbed by the dye and what absorption the dye has in other regions of the spectrum. 26

Q. And the machine mentioned is akin or has a relationship to the spectroscope, which determines the presence of color, but this determines the intensity of the color present; is that it? A. A spectrophotometer is really a spectroscope with a device attached to it for producing such a curve.

Q. It not only determines the presence of the color but determines the intensity of the color present; is that it? A. Yes, and makes a record of it.

Q. And makes a record of it.

The Court: I wanted to get it clear in my mind.

Mr. Smith: I offer in evidence as Exhibits 6-B to 6-I the curves numbered 1 to 8, the curves about which the witness has testified.

(Set of curves was marked Plaintiff's Exhibits Nos. 6-B to 6-I and received in evidence.)

Mr. Smith: I should also like to offer as Exhibit 6-J a Bristol board sheet on which these curves have been transposed so that it is easier to read them, in one sheet.

The Court: I see. That represents all the curves that have been heretofore mentioned, from 6-B to 6-I. In other words, 6-J is a composite picture?

Mr. Smith: 6-J is a composite picture of 6-B to 6-I.

(Composite curve sheet was marked Plaintiff's Exhibit No. 6-J and received in evidence.)

By Mr. Smith:

27 Q. Dr. Vittum, will you refer to these curves and explain what the dotted curves are? A. Each one of these curves contains two separate curves, a dotted curve and a solid-line curve. The dotted curve, as you will see, is identical in all the diagrams, and that represents the one Fischer dye image that we were able to obtain, namely, the dye from 1-naphthol-4-sulfonic acid. The solid-line curves represent the various Schinzel dyes, each of which contains the sulfonamide linkage.

Q. What comparison do these curves show between the Schinzel dyes and the Fischer dye? A. These curves show that the majority of the Schinzel couplers are superior in their light-absorbing characteristics to the Fischer dye.

Q. What region on those charts should theoretically be absorbed for purposes of natural-color photography? A. For natural-color photography the ideal cyan dye would be one that absorbs completely the red end of the spectrum, namely, that represented on these diagrams as falling between 600 and 700. The theoretical dye should also absorb none of the blue region—that is, from 400 to 500—nor the green region, which is from 500 to 600.

Q. And are the Schinzel dyes better with respect to red light absorption than the Fischer dye? A. Yes, in nearly every case one can see a definite advantage with respect to red absorption for the Schinzel dyes.

Q. Did you determine the composition of these dyes? A.
28 Yes, for some of the dyes we did. On our tests it was rather surprising that one was able to obtain a dye image from

1-naphthol-4-sulfonic acid, since all of the other sulfonic acid couplers as described by Fischer gave dyes which were readily soluble in the developer solution and washed out, leaving no dye image.

By the Court:

Q. Well, now, 1-naphthol-4-sulfonic acid is one of the Fischer couplers; is that right? A. Yes; that is the one Fischer coupler.

Q. That is the one that you had the best results with? A. Yes, and it was rather surprising that that one coupler should yield a dye image and all of the other members of that class failed to. That pointed rather clearly, we thought, to the possibility that the Fischer dye did not contain a sulfonic acid; that is, that the sulfonic acid group was eliminated from the coupler molecule during the dye formation.

So we set about to establish that point. The dye was prepared outside of the photographic layer—that is, in solution—and was then subjected to the regular sort of qualitative organic analysis for the presence of the sulfur atom, and we found that the dye did not contain sulfur. Similar tests were made then upon a number of the Schinzel type couplers, and as I recall, there were four or five, and they all did contain sulfur.

Q. In some form? A. Yes, indicating that the sulfonamide image was not lost during the coupling reaction.

By Mr. Smith:

Q. Then those tests showed that the single Fischer coupler which did produce a dye did so by reason of losing its sulfonic acid group during coupling; is that right? A. That is right. 29

* * * *

Q. Did you request any complete analysis of these dyes? A. Yes. We were not completely satisfied with the results of our experiments here. We had rather limited facilities in our laboratory for the manufacture of dyestuffs, as such, and we could not feel too sure that the results were entirely reliable,

so we asked Dr. Weissberger to do really careful quantitative experiments to establish the constitution of this Fischer dye.

* * * *

- 30 Q. Did you make any tests on multilayer material using the Schinzel dyes and the Fischer dye? A. Yes. I might say that in some of our earlier tests we had observed that the Fischer dye was not laid down in very large quantities—that is quantities comparable with those from the Schinzel couplers—unless one used extreme conditions. That is, it is possible to modify conditions to get greater or less amounts of dye.

By the Court:

Q. I do not understand that statement. A. When one used a standard sort of procedure for the preparation of a dye image, the Fischer coupler, 1-naphthol-4-sulfonic acid, yielded a dye in considerably less quantity—that is, density—than we got from the Schinzel couplers.

Q. I see. A. And in order to get comparable dye images—that is, those images absorbing about equal quantities of red light—we had to use a stronger developer formula to obtain that from the Fischer coupler. That led us to considering the usability of the Fischer coupler, 1-naphthol-4-sulfonic acid, in regular 3-color photographic processes.

May I point that out there (indicating)?

Q. Yes. I was going to suggest that you might take that (indicating an exhibit). Now, as I understand it, this (indicating) is the Fischer result? A. That is right.

- 31 Q. And these here represent the experiments by following the so-called Schinzel process (indicating)? A. That is right.

Q. Can you distinguish between, we will say, number 7 in the Schinzel experiment and 8 in the other? A. Yes.

Q. Talking about the absorption of the red field comparatively? A. Well, it is difficult—

Q. (Interposing)—to understand that there? A. It is difficult to see the exhibit in this way. If one will actually look at

this strip—the Schinzel strip—and this strip (indicating), this has considerably more dye on it than this does.

Q. And that is evidenced by the darkness of the blue; is that what you mean? A. Yes.

Q. The intensity of the blue? A. It absorbs more light. This one (indicating), if you look through it against a white background, has a definite bluish tint. I think if you hold it up and look against the calendar (indicating), it has a definite bluish tint, but it is not a dark blue. I mean it does not absorb nearly so much of the red light as the adjoining strip number 7 there.

Q. How about number 5 of the Schinzel? A. Well, number 5 is not very much better than the Fischer coupler.

Q. How about number 3? A. I cannot see. Will you move that over just a bit?

Q. That is almost green. A. Yes. Well, this is a different hue. That is, that has shifted in its maximum absorption, but I think you will find that it absorbs more of the red light. 32

The Court: I take it the Patent Office statement by Mr. Reynolds makes no bones about the fact that the process by which the coupler is developed—the coupler itself, the production of the dye—is invention, but it merely raises the question with reference to the image.

Mr. Smith: The product; that is right. Claims to the method of producing the dye have been allowed.

* * * *

By Mr. Smith:

Q. In these tests on multilayer material what couplers were used for those? A. We had set up in the laboratory a multilayer color process which employed a cyan coupler of the sulfonamide type. The process was all set up and balanced with two other dyes to yield natural color photography; so we selected that process as the starting point, using that cyan coupler that was in use in that process.

Q. What is this three-color process? Will you explain briefly how that is worked?

33 By the Court:

Q. I should like to have you explain first these multilayer films. A. A multilayer film is a film that is built up by superimposing separate emulsion layers.

Q. As for example? A. As for example, one could have a very thin emulsion layer coated on a support, a film base, which was sensitive to red light and sensitive only to red light; the next layer coated on, superimposed directly on that, would be a thin emulsion layer which was sensitive only to green light; then a third emulsion layer would be superimposed upon those two which was sensitive only to blue light.

Q. Well, now, just how far up did you build this multilayer film? To include all the spectrum? Violet? A. No. Natural color photography works out very nicely if you arbitrarily divide the spectrum into three portions: the blue region, the green region, and the red region.

Q. The three basic primary colors? A. The three basic primary colors, yes. That is called three-color photography and is known to yield—

The Court (interposing). Now I have that. Now will you answer counsel's question?

The Witness: I have forgotten the question.

Mr. Smith: Will you read my question, please?

The Reporter (reading)

“Question. What is this three-color process? Will you explain briefly how that is worked?”

34 The Witness. Well, going on from the composition of the multilayer material, the customary procedure in preparing three-color natural photographs is to develop this multilayer material in such a way that the red-sensitive layer is developed to a cyan image; the green-sensitive layer is developed to a magenta image—that is, red and blue magenta; and the blue-sensitive layer is developed to a yellow image. The color of

the dye image in each case is complementary to the color sensitivity of the layer in which it is placed.

Q. Then that film produces a natural-color image in the three layers; is that right? A. Yes.

Q. Did you use a film of this type in these tests on multilayer material? A. Yes, I did; used a standard commercial natural-color film for this purpose.

By the Court:

Q. That is Kodachrome, is it? A. Kodachrome.

By Mr. Smith:

Q. Will you refer to that sheet (indicating)* and tell me whether that shows the results of your tests? A. This is a sheet bearing the strips made in the tests.

Q. And what are the top strips on the sheet? A. The top two strips are strips in which it has produced the cyan dye image in the bottom layer of the film. The bottom two strips are similar strips in which attempts were made to produce Fischer dyes.

Q. Were all of those strips treated in the same way? A. Those strips were all treated in exactly the same manner.

Q. How did you obtain the image only in the bottom layer of the film? A. The process consists in giving the film composed of the three separate layers an exposure to white light through a step tablet. 35

By the Court:

Q. Through a what? A. Through a step tablet.

Q. You had better explain that. A. That is a device for producing increasing exposures from one step to the next. You can see the dividing lines there (indicating). That merely represents more exposure in one case than in the adjoining steps. This film is then developed in an ordinary black and white developer to produce a silver image in all three layers. The film is next subjected to a red light exposure through the base. Now, the only emulsion layer in that film which is sensitive to red

* Exhibit 7 was indicated.

light is the bottom layer. Therefore, on this second exposure only the bottom layer—

By the Court:

Q. (Interposing) Where is the bottom layer on this? A. Well, you are looking down on the three emulsion layers, and the bottom layer is the one next to the film base.

Q. I see. And do these lines here represent different exposures as you go along? A. Yes, that is right. This is one step, and this is one (indicating). That is why we call it a step tablet.

36 Following the second exposure to red light the film is developed in a color-forming developer forming a cyan dye image. Now, in this second developer only that portion of the film that was exposed to red light develops. The rest of it is all unexposed and does not develop, so you produce thereby a cyan dye image which is restricted to the bottom layer of the film.

Q. Where is that? A. Well, it is all over. You just have more development here (indicating) than here (indicating).

The Court: I see.

By Mr. Smith:

Q. Were all of these strips processed in the same way, except using different couplers? A. Yes. Later on we made further attempts, which were not recorded here, to produce dyes from the Fischer couplers by altering the conditions, but we were not successful in any way.

Q. Then were you unable to obtain any cyan dye in this film using naphthol sulfonic acid? A. Well, in one case—that is, the 1-naphthol-4-sulfonic acid—there was a faint suggestion of a cyan dye, but only very faint.

By the Court:

Q. Now, was this the end result (indicating)? A. That was the end result of these tests.

Q. These photographic images involved in these claims? A. Yes, that is right.

By Mr. Smith:

Q. Was this film that you used here regular commercial film? A. Yes, this was regular Kodachrome 16 millimeter film.

* * * *

Q. Did you proceed from that point to make any actual pictures using the Schinzel couplers and the Fischer coupler? 37
A. Yes, we did. Following these tests we thought it advisable to proceed in a similar manner and continue the processing so as to produce the overlying magenta and yellow dyes, as is normally done in the production of three-color photographs.

Q. How did you produce those pictures? That is, what was the general process you went through? A. The general process was exactly as described for the production of these strips here, except that following cyan development one exposes the top layer to blue light and develops in a color-forming developer yielding yellow dye. Then the middle layer is exposed—that is, 38
the green-sensitive layer is exposed—and the film is subjected to a color-forming developer which produces a magenta dye. Following those three separate development stages—steps—one treats the material to remove the metallic silver from the three different layers, leaving the three superimposed dye images.

Q. Are these the pictures that you produced (indicating)?
A. These are the pictures which we produced.

Q. Do the numbers below those pictures correspond to the numbers on the film of Exhibit 7? A. 1, 3, and 4; yes, they correspond.

By the Court:

Q. In other words, 1 is the Schinzel type, and 3 and 4 are the prior art; is that it? A. Yes, that is correct.

The Court: Are there any objections to them?

Mr. Reynolds: I should like to see them.

(The pictures referred to were shown to Mr. Reynolds.)

Mr. Reynolds: Yes; all right.

Mr. Smith: I offer that, those three pictures, as Exhibit 8.

(Panel containing three pictures was marked Plaintiff's Exhibit No. 8 and received in evidence.)

By Mr. Smith:

Q. Will you explain how these pictures differ from the films of Exhibit 7? A. They differ in two respects: In the first place, they are an actual picture instead of being an exposure through a step tablet; and the second difference is that we have now superimposed three dye images: the cyan dye in the bottom layer, the magenta dye in the middle layer, and a yellow dye in the top layer.

And, oh, I should say also, they are pictures on a paper support rather than upon a film support, as these earlier tests were made.

By the Court:

Q. In other words, they are prints; is that right? A. They are prints instead of transparencies.

By Mr. Smith:

Q. Is the arrangement of the three layers on those prints the same as the arrangement of the three layers in the film of Exhibit 7? A. Yes.

Q. What was the effect of using the naphthol sulfonic acids on pictures 3 and 4 of this exhibit? A. Well, we were unable to obtain a dye of the Fischer type in the bottom layer in anywhere near sufficient quantity to produce a satisfactory color photograph.

By the Court:

Q. And by "satisfactory photograph" I take it you mean photograph No. 1 of Plaintiff's Exhibit 8? A. Yes.

By Mr. Smith:

Q. Did you make any effort to increase the amount of cyan dye that might have been formed using the naphthol sulfonic acid? A. Yes, in the production of these pictures we used the standard cyan developer formula for the production of No. 1, and in the prints 3 and 4 we used five times the coupler concentration that was used in production of print No. 1. That was in an effort to get more cyan dye by using more coupler. 40

Q. Is print No. 1 made on a regular production machine? A. Yes.

Q. Using regular production formulas? A. Yes.

Q. And prints 3 and 4 are identical with that except that the naphthol sulfonic acid is substituted for the sulfonamide coupler; is that right? A. Yes.

Q. And those naphthol sulfonic acids produced no noticeable dye? A. Yes.

Q. Is that right? A. That is right.

Q. What are your conclusions, then, regarding the naphthol sulfonic acids of the Fischer patent? A. The conclusion is that only one of the Fischer couplers—that is, 1-naphthol-4-sulfonic acid—is capable of yielding a cyan dye image at all, and that one yields a dye image in insufficient quantity to be of any value for the production of three-color photographs—natural-color photographs.

Q. What would you say about the red light absorption of the Fischer naphthol sulfonic acid? A. That is shown in our tests to be inferior to the red light absorption characteristics of the Schinzel couplers. 41

Mr. Smith: That closes the direct examination.

Cross-Examination by Mr. Reynolds:

Q. Now, isn't it true that the only difference between the Schinzel invention and that of Fischer resides in the specific dye that is used in the two cases? A. Yes, it is.

Q. That is, the actual steps of using the dye to make a photographic image are the same in each case, are they not? A. Yes.

Q. So that any superiority that Schinzel's picture would have over Fischer's is due solely to the particular dye that is used; isn't that true? A. Yes.

* * * *

ARNOLD WEISSBERGER was called as a witness for and on behalf of the plaintiff and, having been first duly sworn, was examined and testified as follows:

Direct Examination. The Assistant Clerk: And your full name?

The Witness: Arnold Weissberger.

By Mr. Smith:

42 Q. Where do you live, Dr. Weissberger? A. Rochester, New York.

Q. What is your occupation? A. I am a research chemist.

Q. By whom are you employed? A. Eastman Kodak Company.

Q. How long have you been employed by them? A. Since August, 1936.

Q. What is your particular work as a research chemist? A. I am working on couplers and on developers and more generally on the chemistry of dye-forming color photographic processes.

Q. What are your educational qualifications as a chemist? A. I studied chemistry from 1918 to 1924 at the Universities of Munich and Leipzig. I took my Ph.D. degree in 1924 in Leipzig. I had become instructor in chemistry in Leipzig in 1923. In 1928 I became privatdocent: assistant professor.

By the Court:

Q. Assistant professor; put it that way. A. Yes. And I was elected to professorship in 1933. This election was not confirmed by the Ministry, which by that time was Nazi and did not confirm my appointment. I then was a research fellow on the invitation of the University of Oxford in England from 1933 to 1936, when I took up employment with Eastman.

By Mr. Smith:

Q. What experience have you had in the preparation of couplers or color formers? A. A short time after I came to Rochester I became interested in the couplers and in the dye formation, and in October, 1938, I was put in charge of the laboratory which prepared the couplers and does the work on the dye-forming color photographic processes. 43

Q. Do you know about how many couplers have been prepared by you or under your direction? A. The total amount of compounds which we made is more than three thousand, and it is a fair estimate to say that about two thousand of those were intermediates for couplers, and about a thousand couplers proper.

Q. Did you receive any request from Dr. Vittum for an analysis of the dye from 1-naphthol-4-sulfonic acid? A. I did.

Q. And did you proceed with that analysis? A. Yes.

Q. Will you tell us briefly what that analysis consisted of? A. The question was what dye is formed from 1-naphthol-4-sulfonic acid. In some preliminary tests in which we used a commercially available 1-naphthol-4-sulfonic acid we found that the final yield of a pure dye was very small: on the order of maybe two to five percent. We were not satisfied with that result because there was a possibility that the commercially available naphthol sulfonic acid contained an impurity to that amount, so that what we really got was not the product of the 1-naphthol-4-sulfonic acid but of some byproduct of the technical material.

We therefore proceeded to make a very pure naphthol sulfonic acid, and we tested the purity of this compound by the for- 44

mation of salts, which are very fully characterized and described in the literature, and by an analysis. Our naphthol sulfonic acid was shown by these tests to be of high purity.

We then dissolved this naphthol sulfonic acid in alkali, added the developer which is used in the color photographic processes, and oxidized this developer. Upon this oxidation of the developer the oxidized developer immediately combined with the naphthol sulfonic acid, and the blue cyan dye was formed.

This dye was extracted by chloroform, and at that point I felt already very sure that the dye would not contain the sulfonic acid group any more, because the extraction with chloroform would not have proceeded as smoothly as it did if the sulfonic acid group would have remained in the dye, that is, if it was present in the dye. The dye was then isolated.

By the Court:

Q. When you say "extracted" what do you mean chemically by that? A. You have an aqueous solution of the dye, and you add a layer of chloroform which is not mixed with this aqueous solution or aqueous suspension, and you shake this mixture so that you get a very intimate contact of little droplets of chloroform with the aqueous solution. Then the chloroform settles down, and the dye is now contained in the chloroform.

Q. In other words, you are using the chloroform more or less as a reagent? A. As an extracting agent.

45 Q. Extracting agent? A. To catch the dye out of this aqueous suspension. Then the chloroform was evaporated, and a solid was obtained which had a melting point—the melting point is used to characterize organic materials—which was not very sharp; but on recrystallization—that means the material was dissolved and then left crystallizing out—we obtained a pure dye.

This dye was analyzed. It had a sharp melting point. It was analyzed, and the analysis showed that it did not contain any sulfur. And the analysis of the dye indicated that this dye obtained from 1-naphthol-4-sulfonic acid—was identical with the dye which one obtains from 1-naphthol itself. We then pre-

pared this dye which is obtained from 1-naphthol not containing sulfonic acid and compared the two dyes, and these two dyes were strictly identical.

Q. So that the sulfonic acid was not necessary at all? A. It was not necessary at all. It was eliminated in the dye formation. And to make absolutely sure that our naphthol sulfonic acid did not contain a trace of naphthol which could have given the dye, we subjected our naphthol sulfonic acid to a so-called steam distillation. That is a process in which you suspend or dissolve the chemical in water and then blow steam through this water. The steam is collected, and volatile compounds are carried over by the steam. Alpha naphthol, which was the impurity for which we had to watch out, is easily carried over by steam, and we did not get any trace of alpha naphthol. However, we showed then that the addition of only .02% of alpha naphthol would have been easily detected.

Q. By the steaming process? A. By the steaming process. 46

By Mr. Smith:

Q. Is this sulfur analysis that you made a standard method of analysis? A. Yes.

* * * *

Q. Was it your conclusion, then, from these tests that you made, that the dye from 1-naphthol-4-sulfonic acid disclosed in the Fischer patent contained no sulfur or sulfonic acid? A. That is right.

* * * *

Mr. Smith: I should like to offer in evidence four 47
copies of patents here. They are not offered to affect
at all the anticipatory value of the case but merely to
show the type of claims that have been granted by the
Patent Office in prior cases.

Do you have any objection Mr. Reynolds?

Mr. Reynolds: No. Give me the numbers of them, will you, please?

Mr. Smith: They are in the back of this book that I gave you.

Mr. Reynolds: All right.

(Patent to Mannes, et al., No. 2,115,394, was marked Plaintiff's Exhibit 11-A and received in evidence.)

(Patent to Mannes, et al., No. 2,126,337, was marked Plaintiff's Exhibit 11-B and received in evidence.)

Pltf. Ex. No. 1
 Specification
 of
 United States Patent Application
 of
 Karl Schinzel
 of
 Zurich, Switzerland
 for
 "PHENOLIC AND NAPHTHOLIC COUPLERS CONTAINING
 SULFONAMIDE GROUPS"
 Serial No. 263,945, filed March 24, 1939

This invention relates to photographic color forming compounds and more particularly to phenolic or naphtholic coupler compounds containing a sulfonamide group.

This application is a continuation in part of my application Serial No. 151,811, filed July 3, 1937.

The formation of colored photographic images by the use of a primary aromatic amino developing agent, which couples with a color forming compound on development, has been the subject of prior patents. Fischer British patent 15,055/1912 discloses phenols and naphthols as coupler compounds which are used with p-phenylenediamine couplers. These coupler compounds react with the developing agent during photographic development to form colored photographic images. The dyes formed in this way are insoluble in water and in the ordinary photographic developing and fixing baths although the silver images formed simultaneously with them may be removed from the photographic layer.

Many of the phenolic and naphtholic coupler compounds hitherto used are not sufficiently soluble in the developing so-

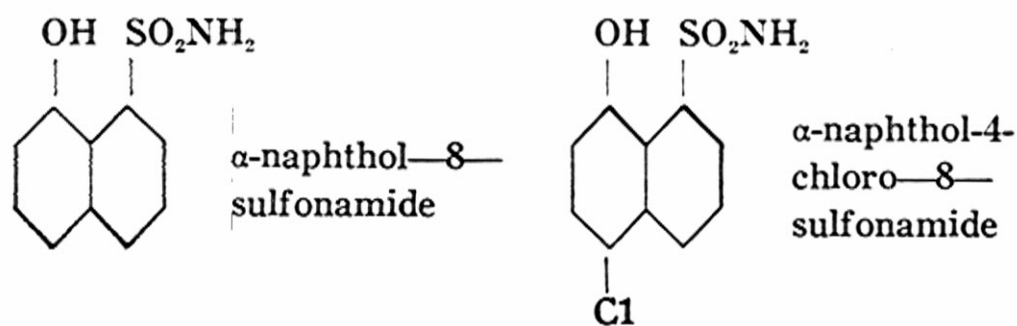
lution to enable them to be incorporated in sufficiently large amounts and some of them also tend to produce cloudy or hazy dye images. For these reasons the images obtained do not always have as high dye density as desired and the resulting picture is not clearly transparent.

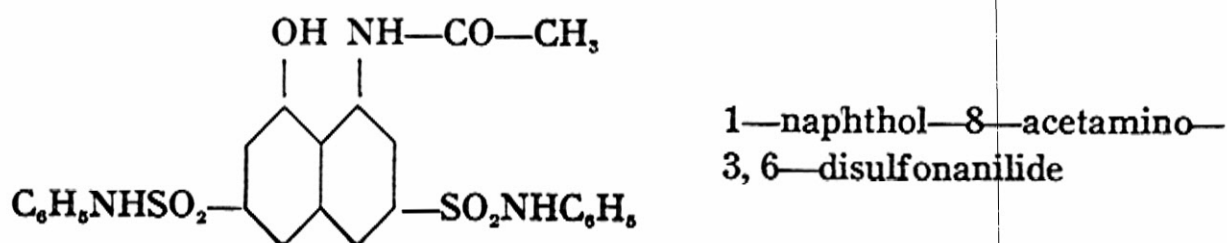
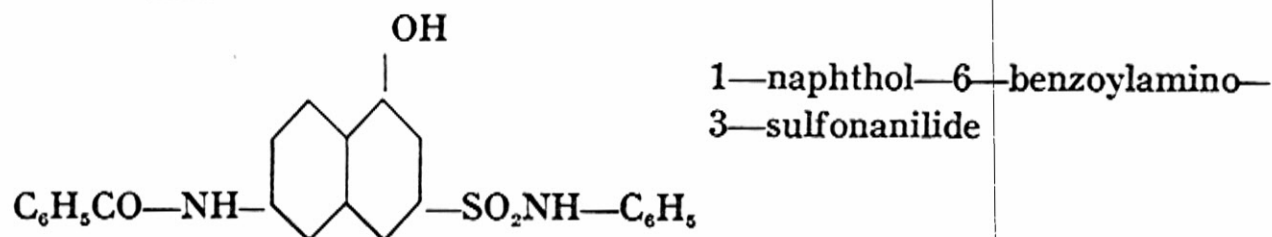
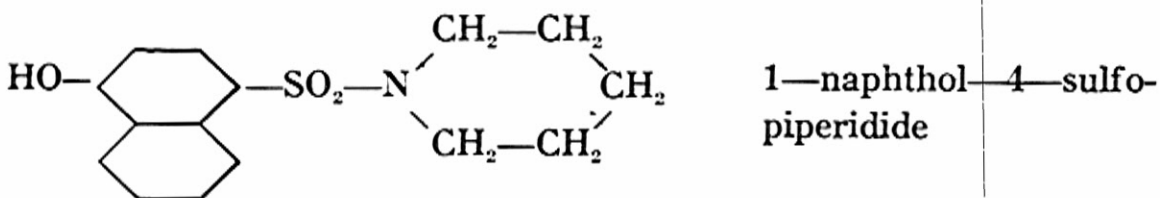
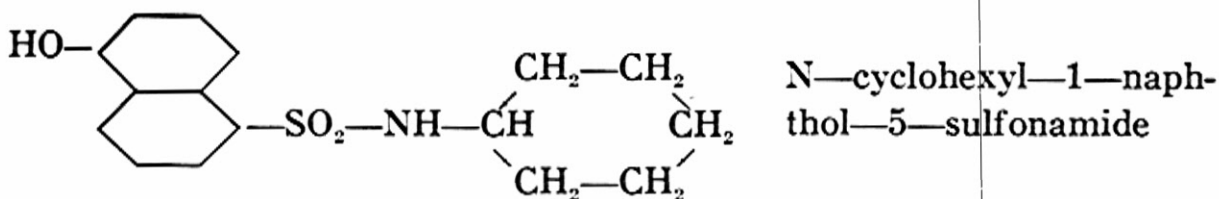
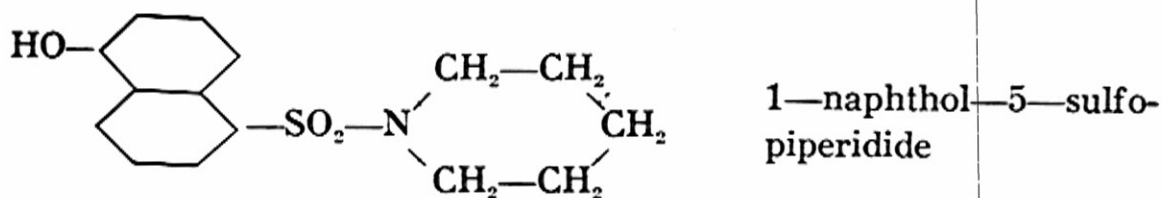
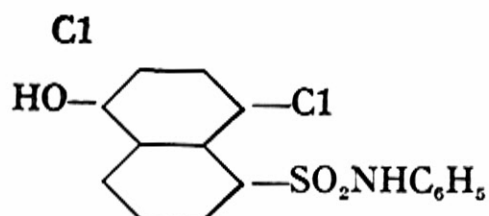
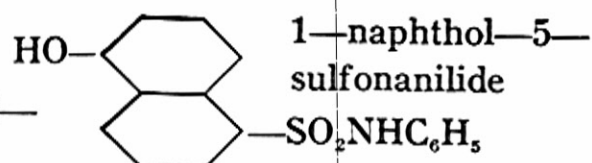
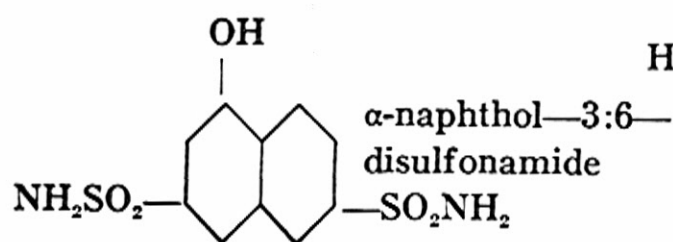
It is, therefore, an object of the present invention to provide novel photographic coupler compounds having desirable characteristics. A further object is to provide photographic couplers which are highly soluble in developing solutions. A still further object is to provide photographic couplers which produce transparent dyes on photographic development. A still further object is to provide coupler compounds which form dyes of desirable transmission characteristics for multi-color photography.

These objects are accomplished by using as couplers phenolic or naphtholic compounds containing at least one sulfonamide group.

The compounds preferably used as couplers according to my invention are α -naphthols containing a sulfonamide group ($-\text{SO}_2\text{NH}_2$). The naphthols may contain substituent groups in the rings and the amino group of the sulfonamide substituent may also be substituted at one or both of the hydrogen atoms. Two or more sulfonamide groups may be present in the compound although the position ortho or para with respect to the hydroxyl group of the naphthol should preferably be free, or substituted with a replaceable group, since it appears likely that the coupling occurs in one of these positions.

Examples of coupler compounds suitable for use according to my invention are as follows:





In place of the α -naphthols containing a sulfonamide described above, I may also use B-naphthols or phenols. These compounds may contain substituent groups in the ring or rings of the phenolic or naphthoic portion of the molecule as illustrated above or one or both hydrogen atoms of the NH_2 group of the sulfonamide may be substituted as indicated in the above examples.

The following example, which is illustrative only, indicates a developing solution which may be used according to my invention.

A.

dimethyl-p-phenylenediamine sulfate	2.5 grams
sodium sulfite anhydrous	2 grams
sodium carbonate anhydrous	20 grams
potassium bromide	1 gram
water to	1000 cc.

B.

1-naphthol—5-sulfonanilide	2 grams
isopropyl alcohol	100 cc.

For use, B is added to A.

In the foregoing examples, I have described adding the coupler compound to the developing solution itself. However, the coupler compound may be incorporated in the photographic layer prior to exposure and the colored image formed by development in the primary aromatic amino developing solution. Special dispersing agents may be used for incorporating the coupler compound in the emulsion and in certain cases the coupler compound may be absorbed or adsorbed to the sensitive salt or may be combined with the sensitive silver salt as a chemical combination. In the case of a multi-layer photographic film in which the color-forming compounds may be incorporated in one or more layers of the film, it may be necessary to take special precautions to prevent wandering of the coupler compound from the sensitive layer in which it is incorporated.

The aromatic amino developing agents used with the coupler compounds of our invention include the mono, di and tri-aminoaryl compounds and their derivatives formed by substitution in the amino group as well as in the ring, such as alkylphenylenediamines and alkyltoluylenediamines. These compounds are usually used in the salt form, such as the hydrochloride or the sulfate, which are more stable than the amines themselves. Suitable compounds are diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediaminehydrochloride, and dimethyl-p-phenylenediaminesulfate. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these compounds have an unsubstituted amino group which enables the oxidation products of the developer to couple with the color forming compounds to form a dye image.

My development process may be employed for the products of colored photographic images in layers of gelatin or other carrier, such as collodion organic esters of cellulose or synthetic resins. The carrier may be supported by a transparent medium such as glass as a cellulose ester or a non-transparent reflecting medium such as paper or an opaque cellulose ester. The emulsion may be coated as a single layer on the support or in the case of a transparent support as superposed layers on one or both sides of the support. The superposed layers may be differentially sensitized and the dyes formed therein by coupling may be bleached by an oxidizing agent such as chromic acid plus KBr to colorless soluble compounds. The destruction of the dye in this way does not destroy the silver image and a silver image may be developed, bleached and developed to color a number of times, thus permitting the formation of natural color images and superposed layers as described, for example, in Mannes and Godowsky U. S. patent No. 2,113,329.

The examples and compounds set forth in the present specification are illustrative only and it is to be understood that my invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. A color-forming photographic developer comprising an aromatic amino developing agent and a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

2. A color-forming photographic developer comprising an aromatic amino developing agent and a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

3. A color-forming photographic developer comprising a paraphenylenediamine developing agent and a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

4. A color-forming photographic developer comprising a paraphenylenediamine developing agent and a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

5. A color-forming photographic developer comprising an aromatic amino developing agent and a coupler compound comprising α -naphthol-8-sulfonamide.

6. A color-forming photographic developer comprising an aromatic amino developing agent and a coupler compound comprising α -naphthol-3:6-disulfonamide.

7. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

8. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a

coupler compound comprising an α -naphthol containing at least one sulfonamide group.

9. A photographic image comprising a dye formed by the coupling of the development product of a paraphenylenediamine developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

10. A photographic image comprising a dye formed by the coupling of the development product of a paraphenylenediamine developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

11. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-8-sulfonamide.

12. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-3:6-disulfonamide.

13. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises exposing it and developing it with an aromatic amino developing agent containing a primary amino group in the presence of a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

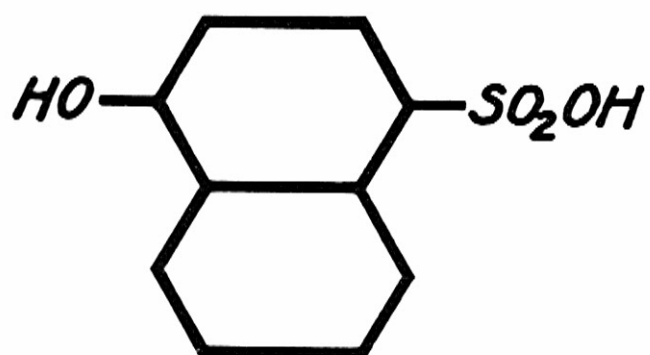
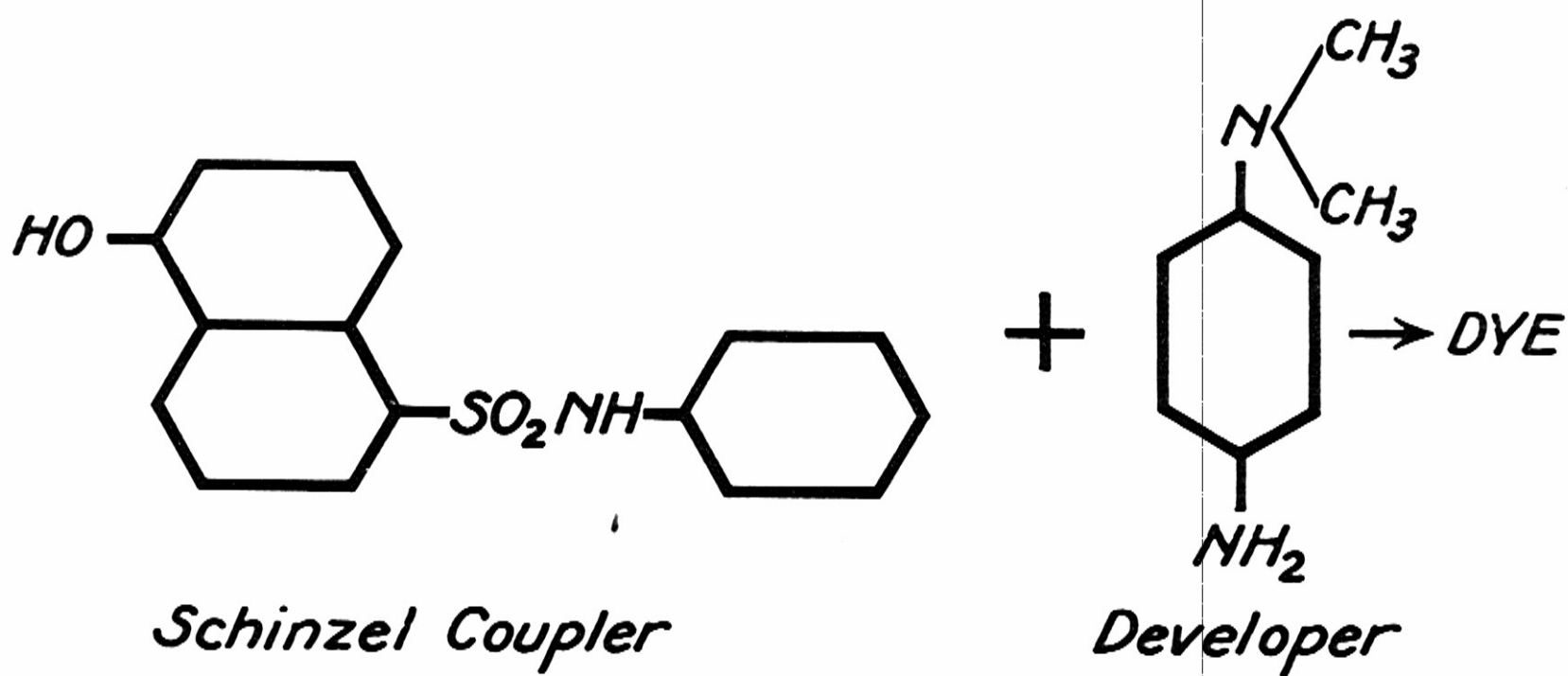
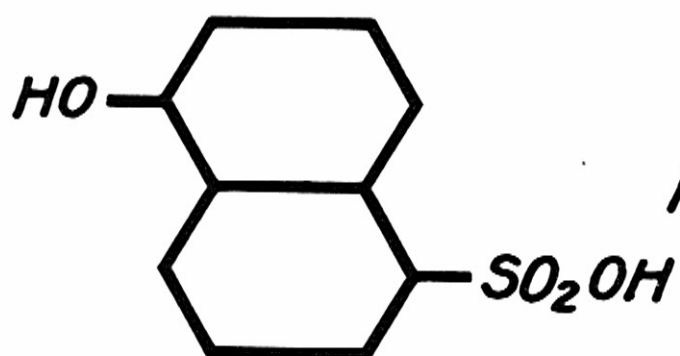
14. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer, which comprises exposing it and developing it with an aromatic amino developing agent containing a primary amino group in the presence of an α -naphthol containing at least one sulfonamide group.

15. A photographic emulsion for forming colored images comprising a carrier containing a sensitive silver halide and a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

16. A photographic emulsion for forming colored images comprising a carrier containing a sensitive silver halide and a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

17. A color-forming photographic layer comprising a gelatino-silver halide emulsion containing a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

18. A color-forming photographic layer comprising a gelatino-silver halide emulsion containing a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

*1-Naphthol-4-Sulfonic Acid**1-Naphthol-5-Sulfonic Acid*

Pltf. Ex. No. 3-A

KODAK PARK WORKS
EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

January 30, 1940

Mr. R. F. Smith
Patent Department
State Street
Dear Mr. Smith:

In accordance with your recent request, we have conducted experiments to compare the results obtained from naphthol-sulfamide couplers on the one hand, and naphthol sulfonic acids on the other. As you will recall, these data were to be used in an attempt to overcome the objections of the examiner to certain claims in the Schinzel sulfanilide coupler application.

Three sets of film strips made in these tests are being sent with this letter. The method of preparation of the strips was briefly the following: 16-mm Cine-Positive film was exposed under controlled conditions behind a step tablet on a continuous drum-printer. Short lengths of this exposed film were then developed in the various color-forming developers for ten minutes, washed five minutes, then subjected to the usual ferricyanide and hypo baths to remove silver and undeveloped silver halide. Finally, the strips were given a wash of ten minutes, and dried. The temperature of all the baths was 70°F. All of the developers were compounded according to the following formula:

8-Amino-5-diethylaminotoluene hydrochloride	2 grams
Sodium sulfite (anhydrous)	1 gram
Sodium carbonate monohydrate	50 grams
Potassium bromide	1 gram
Coupler	2 grams
Sodium hydroxide (10% solution)	10 cc.

The film strips are numbered according to the coupler employed, as follows:

1. 1-Naphthol-5-sulfonic acid
2. 1-Naphthol-5-sulfanilide
3. 2, 4-Dichloro-1-naphthol-5-sulfanilide
4. 1-Naphthol-5-sulfopiperidide
5. N-Cyclohexyl-1-naphthol-5-sulfamide
7. 1-Naphthol-4-sulfonilide
8. 1-Naphthol-4-sulfonic acid
9. 1-Naphthol-5-nitro-4-sulfonic acid
10. 1-Amino-8-naphthol-4-sulfonic acid

Thus, couplers 1, 8, 9, and 10 are examples of the broad group of naphthol sulfonic acids disclosed by Fischer, and the remainder are examples taken from the Schinzel application. Examination of the strips shows that of the Fischer couplers, only No. 8, 1-naphthol-4-sulfonic acid, gives a usable dye image, the others giving rise to dyes which are so soluble that they wash out of the gelatin layer. It is further seen from the strips that the dye from 1-naphthol-4-sulfonic acid is definitely inferior in color characteristics to those from the Schinzel couplers.

Yours very truly,
(Signed) P. W. Vittum
Research Laboratories

PWVittum:VW
cc: Patent Dept. (1)

Pltf. Ex. No. 4

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

May 27, 1941

Dr. P. W. Vittum, Kodak Park:

In connection with the evidence which you have agreed to prepare for use in the civil suit based on our Schinzel U. S. application 263,945, I am enclosing a copy of the U. S. specification as it was filed.

You agreed to obtain any specific couplers listed on page 2 and 3 which are not already available and which you think would produce satisfactory colors, and also to prepare absorption curves for these couplers. In the preparation of these curves it would be advisable to use the developer formula disclosed on page 3 of the specification if possible. You have already sent us developer strips for the last four couplers on page 2 of the specification.

In addition I suggest that you might find out as much as possible about the comparison of these couplers with the Fischer sulfonic acid couplers (1, 8, 9, and 10 of your letter to us of January 30, 1940). If the stability of any of the dyes formed from the couplers of the present application is better than that of the Fischer dyes, this should be noted.

You also agreed to obtain data regarding the formula of the dye formed from 1-naphtha-4-sulfonic acid, showing that the sulfonic acid group is split off on dye formation.

(Signed) R. Frank Smith

Patent Department

RFS:RB

Enc.

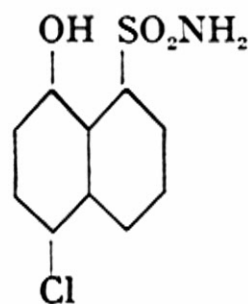
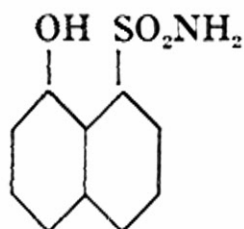
Pltf. Ex. No. 5a

Sept. 16, 1941

In accordance with letter of May 27, 1941 from R. F. Smith, tests were made with the couplers described in the above application, in comparison with certain sulfonic acid couplers of the α -naphthol series as disclosed by Fischer.

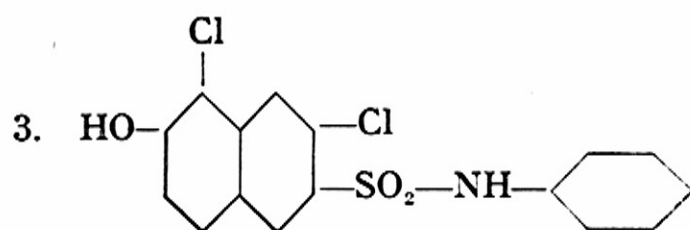
Samples of the Schinzel couplers were prepared for us in the laboratory of A. Weissberger, and samples of the Fischer couplers were obtained from the regular list of the Synthetic Organic Chemicals department.

Dr. Weissberger was unable to prepare the following two couplers from the Schinzel list:

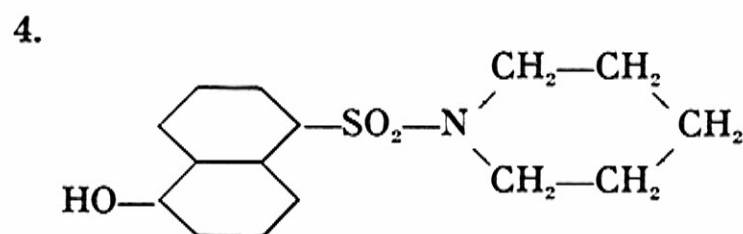


The following is a list of the couplers tested:

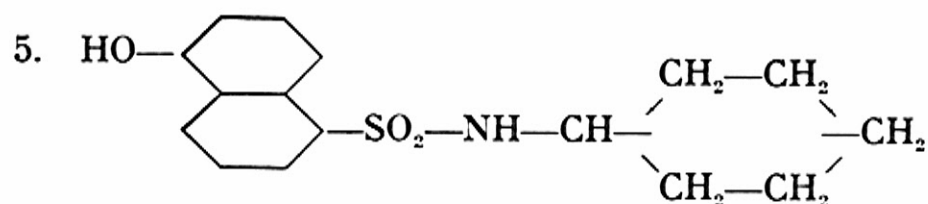
1. 1-naphthol-3, 6-disulfonamide
B-922-88
2. 1-naphthol-5-sulfanilide
WP 2553 B-929-65



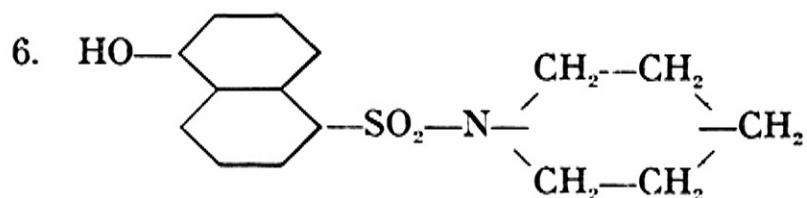
2, 4-Dichloro-1-naphthol-5-sulfanilide
WP 2648 B925-93



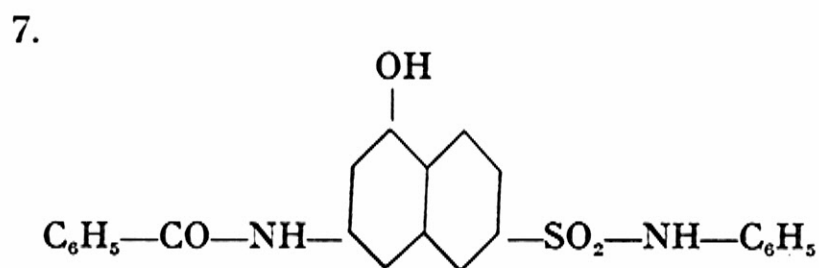
1-Naphthol-5-sulfopiperidide
WP 2649 B925-89



N-Cyclohexyl-1-naphthol-5-sulfonamide
WP 2641 B-925-90

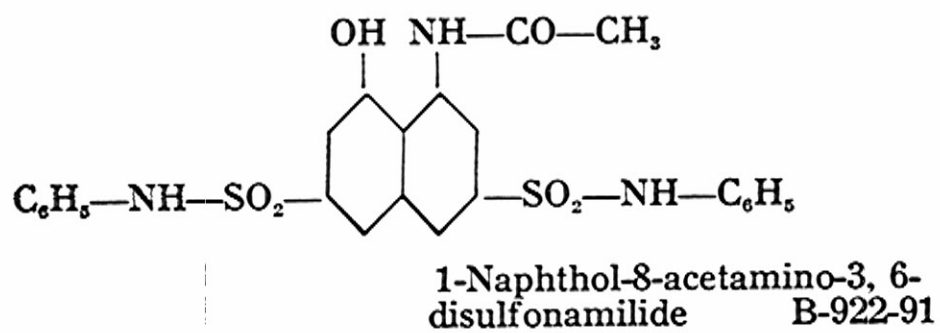


1-Naphthol-4-sulfopiperidide
B 922-84

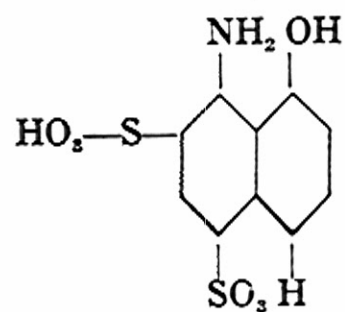


1-Naphthol-6-benzoylamino-3-sulfonanilide
B 922-83

8.

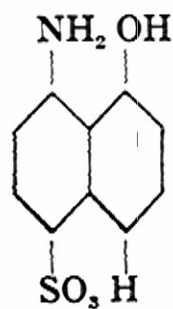


9.



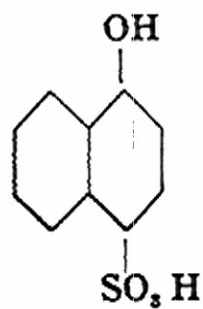
1-Amino-8-naphthol-2, 4-disulfonic acid
Cab. No. T 2800

10.



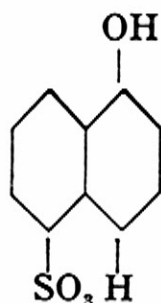
1-Amino-8-naphthol-4-sulfonic acid
Cab. No. T 2797

11.



1-Naphthol-4-sulfonic acid
Cab. No. T 232

12.



1-Naphthol-5-sulfonic acid
Cab. No. T 2807

Couplers 1 to 8 are those from the Schinzel application, while 9 to 12 are α -naphthol sulfonic acids of the general type disclosed by Fischer.

Preliminary tests were made with these couplers to compare their development characteristics, and it was found that with some of them, used in the formula given by Schinzel, the dye images were quite weak. Since it was considered desirable to obtain nearly equal dye describies with all the couplers, a stronger developer solution was used for those giving low describies with the Schinzel formula. The formulas employed were as follows:

I. Schinzel Formula

A.	Dimethyl p-phenylenediamine sulfate	2.5 grams
	Sodium sulfite, anhydrous	2 grams
	Sodium carbonate, anhydrous	20 grams
	Potassium bromide	1 gram
	Water to	1000 cc
B.	Coupler	2 grams
	Isopropyl Alcohol	100 cc.
	For use, B is added to A	

II. Stronger Formula

A.	Dimethyl p-phenylenediamine sulfate	2.5 grams
	Sodium sulfite, anhydrous	2 grams
	Sodium carbonate, anhydrous	20 grams
	Potassium bromide	1 gram
	Water to	1000 cc.

B. Coupler	4 grams
Isopropyl Alcohol	100 cc.
10% Sodium hydroxide solution	10 cc.
For use B is added to A	

For the preparation of the film strip samples, strips of cine-positive film on safety support were exposed behind a step tablet having wide ($1\frac{1}{2}$ ") steps under controlled conditions. These strips were developed in the various developer solutions at 70° C. for the correct times, previously established by test to yield the desired dye desirity in one of the steps of each strip. After development, the strips were washed 5 min. in running water, then treated in the usual ferricyanide-bromide and hypo baths to remove silver and silver halide. The strips were finally washed for 10 min. and dried.

The following table summarizes the conditions used for the various developer solutions. The coupler numbers correspond to those in the list on pages 91 to 93.

Coupler	Developer Formula Used	Time of Dev. 70° C.	Results
1.	I	20 min.	Dye too soluble and washes out.
2.	I	10 min.	
3.	I	14 min.	
4.	I	10 min.	
5.	I	5 min.	
6.	II	25 min.	Dye density still too low to give good curve.
7.	II	15 min.	
8.	II	15 min.	
9.	II	15 min.	
10.	II	15 min.	
11.	II	15 min.	Satisfactory
12.	II	15 min.	No dye

As indicated, the dye from Coupler 1 was too soluble and washed out, so a repeat test was made using this coupler with diethyl-p-phenylenediamine. The dye resulting in this test was less soluble and a better dye image was obtained.

The strips prepared in the above tests were given to Mr. Richardson who obtained spectrophotometric curves using the automatic recording spectrophotometer.

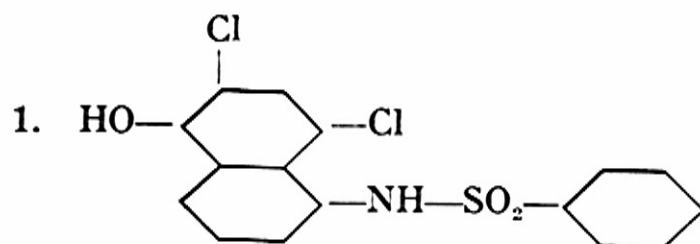
(Signed) P. W. Vittum

Pltf. Ex. No. 5c

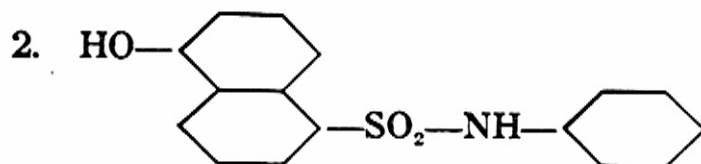
May 1, 1942

Comparison of Cyan Couplers for Bottom Layer Kodachrome Film

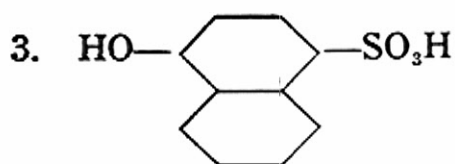
Continuing the experiments described on pages 91-96, this book, it was thought desirable to compare some of the cyan couplers for their ability to produce satisfactory dye images in one layer of a practical multi-layer material. The following couplers were available in sufficient quantity for making such a test:



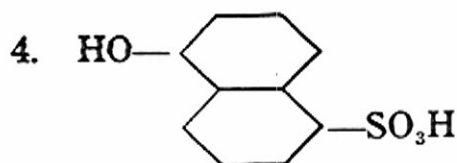
2, 4-Dichloro-5-benzene sulfonamide-1-naphthol



1-Naphthol-5-sulfanilide



1-Naphthol-4-sulfonic acid



1-Naphthol-5-sulfonic acid

Regular daylight Kodachrome 16 mm. film was exposed behind a neutral step tablet on a continuous drum printer, and processed according to the following procedure: (all baths at 70° F)

- 2 min. Hardener
- 10 min. MQ first developer
- 1 min. Rinse
- 3 sec. red light exposure
- 14 min. color development
- 10 min. wash
- 5 min. Ferricyanide
- 5 min. Hypo
- 10 min. Wash, then dry

The formulae for hardener, MQ, ferricyanide, and hypo are those given in the Cine-Kodak Processing Dept. instruction booklet of January 27, 1939. The color developers were prepared according to the formula:

- 3.3g. 2-Amino-5-diethylaminotoluene hydrochloride
- 3.5g. Sodium Sulphite (anhydrous)
- 50.0g. Sodium Carbonate (monohydrate)
- 3.0g. Potassium Bromide
- 0.5g. Potassium Thiocyanate
- 2.0g. Coupler
- 1.0g. Sodium Hydroxide
- 1000 cc. Water

The coupler is dissolved in a solution of the sodium hydroxide in 100 cc. of the water, and this solution then is added to the rest of the solution.

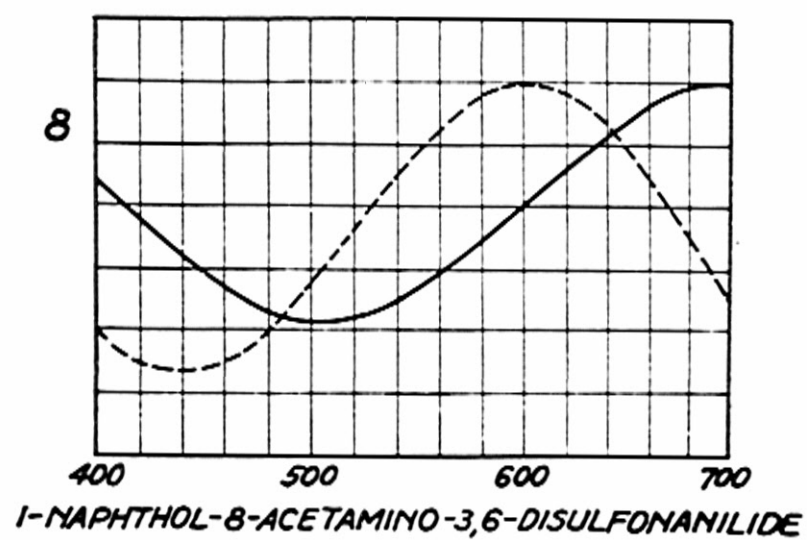
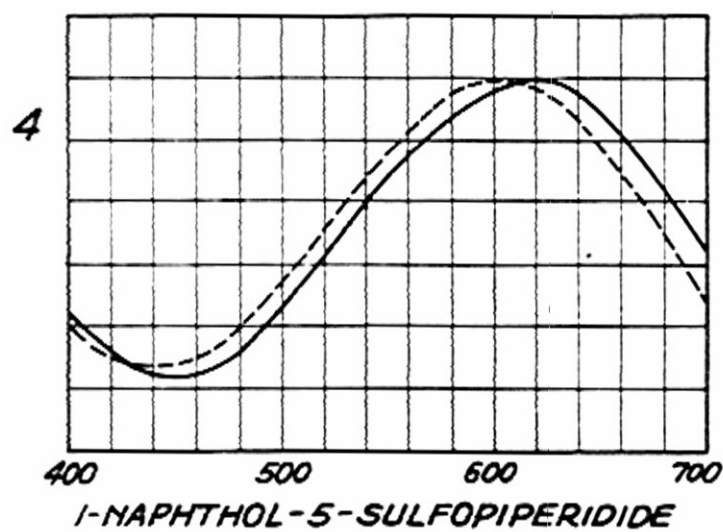
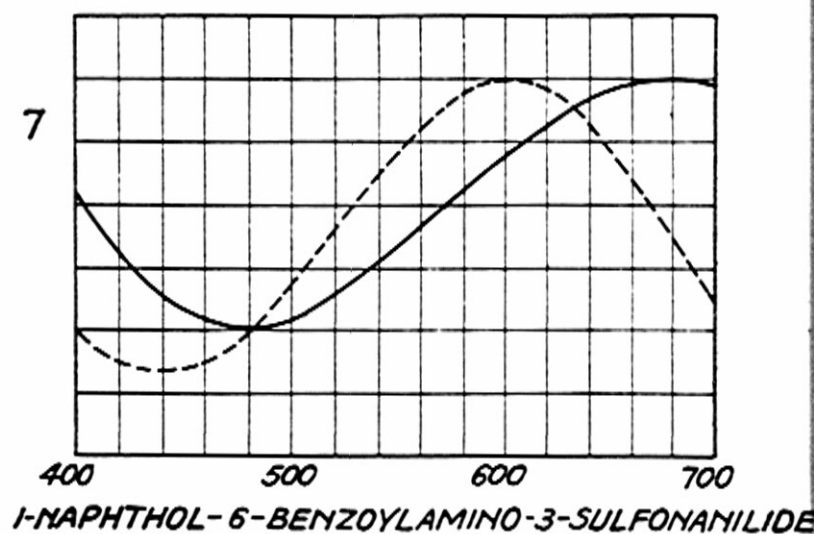
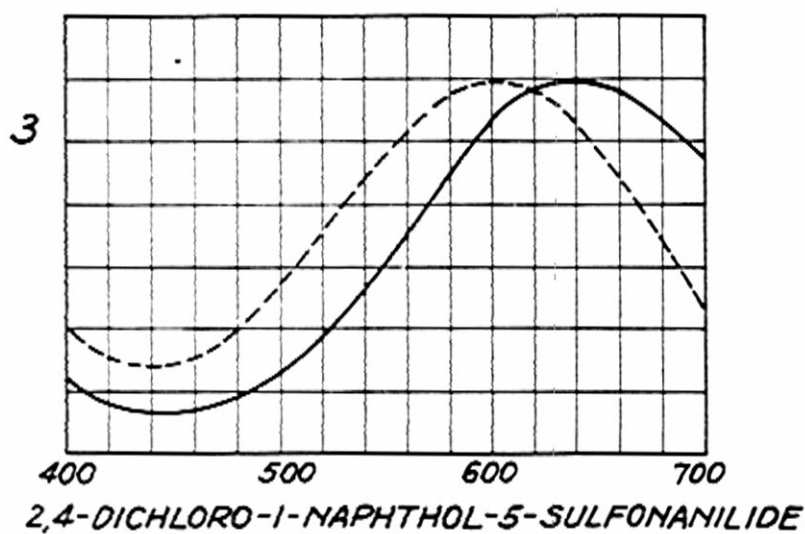
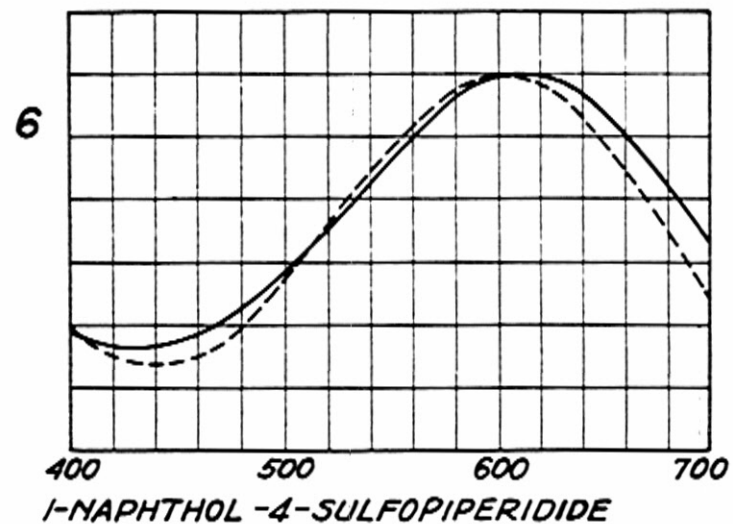
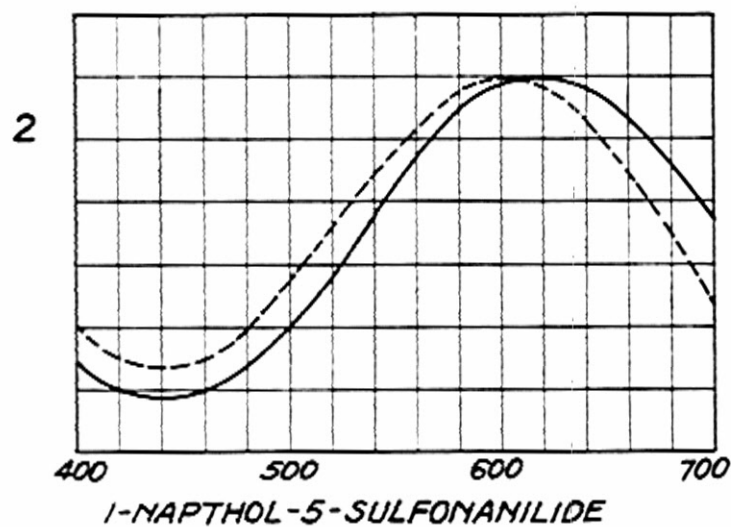
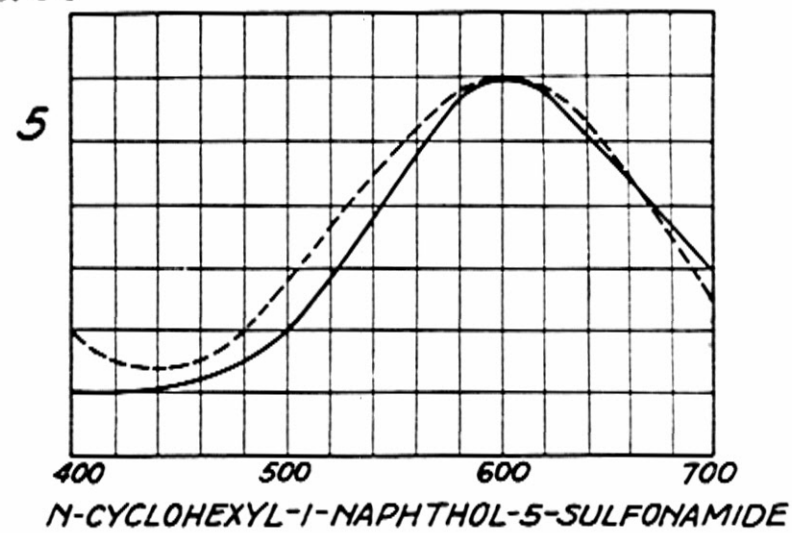
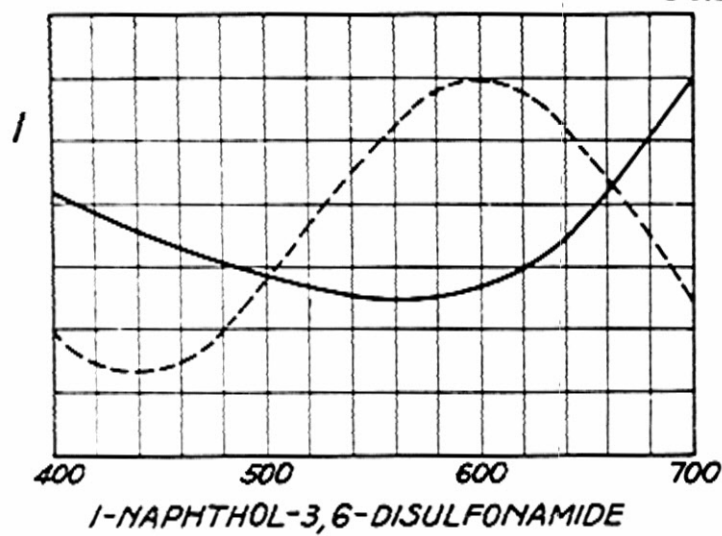
This procedure yields a reversal cyan image which is restricted to the red-sensitive layer of the multi-layer material, since only this layer receives exposure before color development.

Results:

Couplers 1 and 2 by the above procedure gave quite intense dye images, that from No. 1 being more green than that from No. 2. Coupler 3, 1-naphthol-4-sulfonic acid, gave only a trace of blue dye image, while Coupler 4, 1-naphthol-5-sulfonic acid gave an extremely weak greenish-gray image. These results demonstrate the inability of the sulfonic acid couplers (3 and 4) to yield usable dye images in a multi-layer material.

Considering these results with those from earlier tests (see pp. 91-96), one would conclude that the dye from 1-naphthol-5-sulfonic acid is too water-soluble to be deposited as a dye image. With 1-naphthol-4-sulfonic acid, however, the situation is different. This coupler loses its sulfonic acid group during the coupling reaction to yield a dye containing no SO_3H . This coupling reaction, involving the splitting out of the SO_3H , is seen from these tests to be a slow one, since only a small amount of dye is formed. The oxidized developer must in large part be lost in other reactions, such as reaction with sodium sulfite or with itself. It is only under conditions such as those used previously (pp. 91-96) that one gets a reasonable dye image from this coupler. In those earlier tests, a much thicker emulsion layer (Cine-positive film) was used, and a strong developer formula, so that a fairly dense dye image was obtained despite the inefficiency of the coupling reaction. Such conditions could not prevail in a practical multi-layer material.

(Signed) P. W. Vittum



Pltf. Ex. No. 9

Serial No. B-210

Date: 10/30/41

Page No. 01

Dye from 1-Naphthol-4-sulfonic Acid and Developer No. 2

Preparation of Sodium 1-Naphthol-4-sulfonate from: Cain and Thorpe, "The Synthetic Dyestuffs and Intermediate Products," page 343

100 g. of sodium naphthionate hemihydrate and 800 g. of 40% sodium bisulfite solution were mixed, 200 cc. of water were added and the mixture was refluxed over a free flame for 12 hours. At the end of that time no precipitate formed when a sample of the mixture was acidified with dilute (1:1) hydrochloric acid. The reaction mixture was then made alkaline by the addition of 500 cc. of 40% sodium hydroxide and boiled under reflux until no more ammonia was evolved. This required about 12 hours. After cooling, the mixture was poured, with stirring, into 1 liter of concentrated hydrochloric acid and then boiled under reflux for 8 hours to expel the SO_2 . It was then cooled to 0° and the precipitate filtered off. The solid was dissolved in 500 cc. of boiling water, the solution treated with Norit and Darco, filtered, 1 liter of saturated salt solution added,

Page No. 02

and the mixture cooled to 0° . The precipitate was filtered off, washed with a little alcohol and finally with ether. The sodium 1-naphthol-4-sulfonate formed a slightly yellowish crystalline powder containing no water of crystallization. Yield 62 g. (67.5%)

Preparation of the Dye

12.3 g. (0.05 mole) of sodium 1-naphthol-4-sulfonate and 10.5 g. (0.25 mole) of solid sodium hydroxide (95% pellets) were dissolved in 1 liter of water. With stirring, a solution of 10.7 grams (0.05 mole) of 2-Amino-5-diethylaminotoluene monohydrochloride (Developer #2) in 250 cc. of water was

added to the alkaline solution. The free base of the developer precipitated momentarily, but immediately redissolved. A solution of 68 g. (0.2 moles) of potassium ferricyanide in 500 cc. of water was then added portionwise with vigorous stirring and the mixture stirred at room temperature for two hours. A blue dye formed immediately after the

Page No. 03

addition of the ferricyanide but it was colloidal in form and could not be filtered. Acetic acid failed to coagulate it. 200 g. of sodium chloride was dissolved in the mixture and the dye was extracted with chloroform, using one- one liter and two- 500 cc. portions. The combined extracts were washed with water (3- 500 cc. portions) and dried over magnesium sulfate. It was noted that all the blue dye was extracted from the reaction solution by the chloroform. The aqueous liquor was a dirty red-brown in color, and contained no blue dye soluble or otherwise. The dried chloroform solution was evaporated to dryness on the steam-bath, and the sticky, black residue boiled with 400 cc. of 3-A alcohol. Most of it dissolved leaving only a small amount of sticky, dark-brown residue. The solution was treated with Nuchor, filtered and cooled to 0°. No precipitation resulted. The solution was transferred to a crystallization dish and evaporated to dryness on the steam-bath. The at first sticky residue partially solidified on standing. It melted

Page No. 04

over the range 60-90° and weighed 2.5 grams. This is 15.7% of the theoretical yield of 15.9 g.

For purification, the dye was recrystallized from methyl alcohol twice and from 3-A alcohol once. It then formed shining black or very dark purple tablets, m. p. 111.5-112°.

The mixed melting point with an authentic sample of the dye from α -naphthol and developer #2 (m. p. 110-111°) was 110.5-111.5°.

The yield of pure dye was 0.5 g. (20% for the purification).

Mol. wts.	Sodium Naphthionate Hemihydrate	254
	Sodium bisulfite	104
	Sodium 1-Naphthol-4-sulfonate	246
	2-Amino-5-diethylaminotoluene Mono-hydrochloride	214.5
	Sodium hydroxide	40
	Potassium ferricyanide	329.2
	Dye	318

Serial No. B-201

Date: 11/10/41

Page No. 11

Examination of the Dye Obtained from 1-Naphthol-4-sulfonic Acid and Developer #2

The dye gave no test for sulfur by the sodium fusion method. The sodium-1-naphthol-4-sulfonate gave a strong positive test.

Analysis	Calculated for $C_{21}H_{22}N_2O$	Found
	79.20	78.26
	6.97	7.04
	8.80	8.42

To establish the identity of the sodium 1-naphthol-4-sulfonate, a number of aryl amine salts of the acid were prepared. Their melting points, and the melting points recorded in the literature, are given below:

Amine	m. p.	lit. m. p.*
Aniline	184-185°	186°
p-Toluidine	195-196°	196°
p-Anisidine	215-216°	224°
α -Naphthylamine	212-213°	216-217°

*Forster and Watson J. Soc. Chem Ind. 46, 224 (1927)

To establish the fact that the sodium 1-naphthol-4-sulfonate contained no free α -naphthol from which the dye could have been formed, a

sample of the salt was dissolved in water, the solution was acidified with acetic acid, and steam distilled. The distillate gave no dye formation with benzene diazonium chloride solution, indicating the absence of 1-naphthol. A sample to which 0.02% of α -naphthol had been added gave a positive test for α -naphthol in the distillate, when similarly treated.

Pltf. Ex. No. 10

KODAK PARK WORKS
EASTMAN KODAK COMPANY
ROCHESTER, N. Y.

November 11, 1941

Dr. P. W. Vittum
Building 59
Dear Dr. Vittum:

We have oxidized with ferricyanide an alkaline solution containing 1-naphthol-4-sulfonate and 2-amino-5-diethylamino toluene in order to examine whether there results an unsulfonated dye.

1-Naphthol-4-sulfonic acid (Nevile and Winthers acid) was prepared according to the procedure given in Cain and Thorpe, "The Synthetic Dyestuffs and Intermediate Products", 7th Ed., London, 1933, page 343, and the sodium salt precipitated by salting out with a saturated sodium chloride solution. For purposes of identification, the following salts were made:

Salt with p-toluidine

m.p. 195-196° m.p. 196°
according to Foster and
Watson, J. Soc. Chem.
Ind., 46, 224 (1929).

Salt with aniline

m.p. 184-185° m.p. 186-187°
according to above
reference.

The absence of even traces of α -naphthol was ascertained by dissolving part of the product in aqueous acetic acid, blowing steam through this solution and testing the distillate, which was made alkaline with benzene diazonium chloride solution. A reference made with a sample to which 0.02% of α -naphthol had been added gave a positive test for α -naphthol in the distillate.

12.3 g. of sodium-1-naphthol-4-sulfonate was dissolved in 1 l. of water containing 10.5 g. of sodium hydroxide. To this was added with stirring, a solution of 10.4 g. of 2-amino-diethylamino toluene monohydrochloride in 250 cc. of water, and, subsequently, a solution of 66 g. of potassium ferricyanide in 500 cc. of water. A blue dye formed immediately. After stirring for two hours, 200 g. of salt was dissolved in the mixture and the dye extracted with chloroform. The aqueous solution was colorless. The chloroform extracts were washed with water, dried with magnesium sulfate and the solvent was distilled off. The residue was dissolved with 400 cc. of 3-A alcohol, filtered from a small amount of insoluble material, treated with Nuchar, filtered and the alcohol evaporated. 2.5 g. of a sticky, dark-blue residue, softening at 60°, which partially crystallized on standing, was obtained. It was recrystallized from 100 cc. of methanol, yielding 1 g. of dark-purple tablets with a gold lustre of m.p. 106-108°. On repeated recrystallizations, the m.p. was raised to 111.5-112°.

The material, according to melting point and mixed melting point, is identical with the dye obtained from 1-naphthol by a treatment similar to that given above. Analysis calc'd: C, 79.2; H, 6.97; N, 8.8. Found: C, 78.26; H, 7.04; N, 8.42. The lack of sulfur was proved by a fusion of the dye with sodium and the absence of sulfide in the aqueous extract of the fusion product. Hence, 1-naphthol-4-sulfonic acid on oxidation with

ferricyanide in the presence of 2-amino-5-diethylamino toluene at room temperature can eliminate the sulfonic acid group and form a dye identical with the one obtained from α -naphthol. In view of the purity of the starting materials, the yield in our procedure, although small, gives definite proof for this elimination. No attempt was made to increase the yield.

Yours very truly,

(Signed) A. Weissberger

Synthetic Organic Research Laboratory

AWeissberger:GD

cc. to Mr. R. F. Smith, Patent Department

UNITED STATES PATENT OFFICE

2,115,394

PHOTOGRAPHIC COLOR-FORMING COMPOUNDS

Leopold D. Mannes, Leopold Godowsky, Jr., and Willard D. Peterson, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

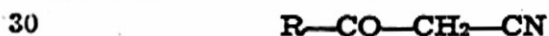
No Drawing. Application October 14, 1936, Serial No. 105,617

12 Claims. (Cl. 95—88)

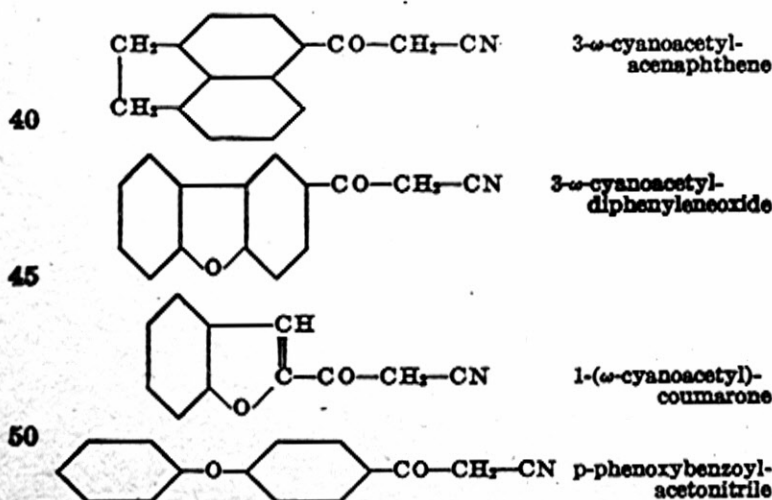
This invention relates to photographic developers and more particularly to compounds which form dyes by coupling with the developing compound on development.

- 5 The method of forming colored photographic images by depositing a colored compound in the photographic layer adjacent the silver image on development has been described in numerous prior patents. The present invention relates to a process in which the color-forming compound is contained preferably in the developing solution, but might also be incorporated in the sensitive material and forms a dye simultaneously and in situ with the development of the silver image by coupling with the oxidation product of the photographic developer. In U. S. Patent No. 2,039,730, granted May 5, 1936, to L. D. Mannes and L. Godowsky, Jr., there is disclosed the use of hydroxylated diphenyl compounds for this purpose. 10 The use of other types of compounds was also described in application, Serial No. 8519, of L. D. Mannes and L. Godowsky, Jr.

We have found that certain organic compounds containing the cyanoacetyl group as a substituent are useful as coupler compounds in photographic developers and form colored images on photographic development. The compounds which we contemplate using have the following general formula:



in which R may be one of the following groups: acenaphthenyl, dibenzofuryl, coumaronyl or phenoxyphenyl. The compounds containing these groups attached to a cyanoacetyl group will have the following formulae:



These compounds when present in a developer solution containing an aromatic amino developing compound coupler with the oxidation prod-

uct of the aromatic amino developing compound form a dye simultaneously with the formation of the silver image. The coupling occurs in each case at the methylene group contained between the carbonyl group and the cyano group of the coupler compound.

The coupler compounds used may be substituted in the aromatic ring with groups including halide, nitro, amino, substituted amino, alkyl, aryl and carboxyl groups. These groups may be substituted in the ring at any position since the ring is not reactive in the coupling to form the dye.

As developing agents we contemplate using the aromatic amino compounds which function as photographic developers. The compounds preferred for this purpose are para phenylenediamine and its substituted derivatives. These developers may be substituted in the amino groups as well as in the ring with alkyl, ester, or halide groups. We prefer to use as developers para phenylenediamine dialkyl substituted in one amino group, the other amino group remaining unsubstituted. These compounds are ordinarily used in the salt form, such as the hydrochloride or sulfate, since these compounds are more stable than the amines themselves. Developing agents which may be used include diethyl para phenylenediamine, monomethyl para phenylenediamine hydrochloride and diethylene para phenylenediamine sulfate.

A developing formula which may be used is the following:

A	
Diethyl para phenylenediamine hydrochloride	gram 1
Sodium sulfite	do 0.5
Sodium carbonate	grams 20
Water	litre 1

B	
Coupler	gram 1
Acetone	cc 50

Add B to A.

The developing agent and the proportions of the ingredients used in the above formula may, of course, be varied. Solvents other than acetone, such as alcohols, may also be used.

The colors formed by the compounds of the present invention on coupling with the oxidation product of the developer are various shades of red and magenta. The colors may, of course, be altered by inserting various substituent groups into the molecule of the coupler compounds.

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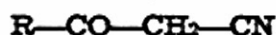
Although we have described our invention with particular reference to the use of the coupling compound in the developing solution itself, our invention is in no way limited to this method.

- 5 As an alternative method, the coupler compound may be incorporated in the photographic layer before development, or before exposure and development. It may be adsorbed to the sensitive silver halide grain or chemically combined with the sensitive salt, or, in some cases, the silver salt of the coupler compound itself, without halide, may exhibit light sensitivity and coupling properties on development.

- Our compounds may be used to form colored photographic images in films plates, or paper, when gelatin or other suitable colloid is used as the carrier for the silver halide constituting the sensitive salt. The emulsion treated to form the colored image may be on one side or on both sides of the support or superposed emulsion layers may be coated on one or both sides of the support. Where a plurality of layers is used the layers may be differently sensitized to form natural colored images on development, according to the process described in application, Serial No. 8,516, filed February 27, 1935, by L. D. Mannes and L. Godowsky, Jr.

What we claim is:

1. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and a coupler compound having the formula



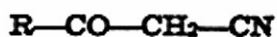
- where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

2. A color-forming photographic developer comprising a dialkyl amino paraphenylene diamine and a coupler compound having the formula



- where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

3. A color-forming photographic developer comprising a diethyl paraphenylene diamine hydrochloride and a coupler compound having the formula



- where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

4. A color-forming photographic developer

comprising an aromatic amino developing compound containing a primary amino group and 3- ω -cyanoacetyl-acenaphthene.

5. A color-forming photographic developer comprising a dialkyl amino paraphenylene diamine developing compound and 3- ω -cyanoacetyl-acenaphthene.

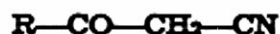
6. A color-forming photographic developer comprising diethyl paraphenylene diamine hydrochloride and 3- ω -cyanoacetyl-diphenylene oxide.

7. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and 1-(ω -cyanoacetyl)-coumarone.

8. A color-forming photographic developer comprising a dialkyl amino paraphenylene diamine developing compound and 1-(ω -cyanoacetyl)-coumarone.

9. A color-forming developer comprising diethyl para phenylenediamine hydrochloride and 1-(ω -cyanoacetyl)-coumarone.

10. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing compound containing a primary amino group with a compound having the formula



where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

11. A photographic image comprising a dye formed by the coupling of the development product of a dialkyl amino paraphenylene diamine with a compound having the formula



where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

12. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer which comprises coupling the development product of an aromatic amino developing compound containing a primary amino group with a compound having the formula



where R is selected from the class consisting of acenaphthenyl, dibenzofuryl, coumaronyl, and phenoxyphenyl groups.

LEOPOLD D. MANNES.

LEOPOLD GODOWSKY, Jr.

WILLARD D. PETERSON.

UNITED STATES PATENT OFFICE

2,126,337

PHOTOGRAPHIC COLOR-FORMING COMPOUNDS

Leopold D. Mannes, Leopold Godowsky, Jr., and
Willard D. Peterson, Rochester, N. Y., assignors
to Eastman Kodak Company, Rochester, N. Y.,
a corporation of New Jersey

No Drawing. Application October 14, 1936.
Serial No. 105,616

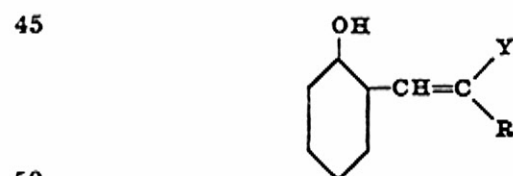
15 Claims. (Cl. 95—88)

This invention relates to photographic developers and more particularly to compounds which form dyes by coupling with the developing compound on development.

5 The method of forming colored photographic images by depositing a colored compound in the photographic layer adjacent the silver image on development has been described in numerous prior patents. The present invention relates to
10 a process in which the color-forming compound is contained preferably in the developing solution, but might also be in the sensitive material, and forms a dye simultaneously and in situ with the development of the silver image by coupling
15 with the oxidization product of the photographic developer. In U. S. Patent No. 2,039,730, granted May 5, 1936, to L. D. Mannes and L. Godowsky, Jr., there is disclosed the use of hydroxylated diphenyl compounds for this purpose. The use
20 of other types of compounds was also described in application, Serial No. 8,519, of L. D. Mannes and L. Godowsky, Jr.

We have found that certain hydroxy styryl compounds are useful as coupler compounds in
25 photographic developers and form colored images on photographic development. The dyes which we contemplate using consist of hydroxy styrenes substituted at the end of the chain opposite to that at which the aromatic nucleus
30 is attached, with an unsaturated or saturated aromatic nucleus or with a heterocyclic nucleus. The hydroxyl group will usually be in the position ortho with respect to the conjugated chain so that the position para with respect to the
35 hydroxyl group is left free for coupling with the oxidization product of the developer. In some cases, however, the coupling may occur in the position ortho with respect to the hydroxyl group and in this case the hydroxyl group may
40 occur in the position para with respect to the conjugated chain.

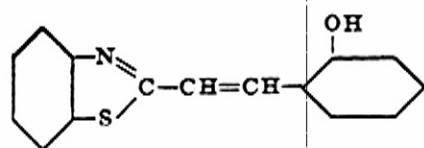
The hydroxy styryl compounds which we use have the following general formula:



in which Y is a hydrogen atom and R is a heterocyclic ring or Y and R together form a heterocyclic ring or an aromatic ring.

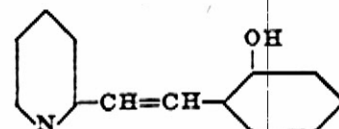
55 The following compounds which we contem-

plate using are compounds in which Y is a hydrogen atom and R is a heterocyclic ring:



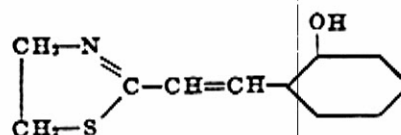
1-(o-hydroxycinnamyl) benzothiazole

5



2-(o-hydroxycinnamyl) pyridine

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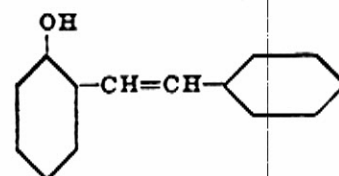


2-(o-hydroxycinnamyl) thiazoline

15

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The following compound is one which may be used in which Y is a hydrogen atom and R is an aromatic nucleus:

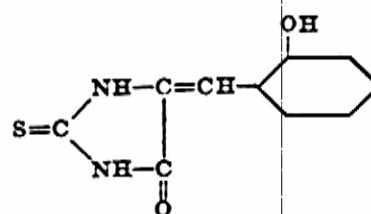


o-styrylphenol

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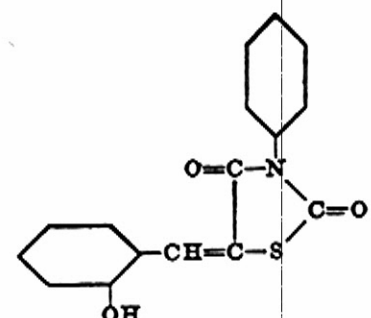
In the following compounds Y and R together represent a heterocyclic ring:



5-(o-hydroxybenzal)-2-thiohydantoin

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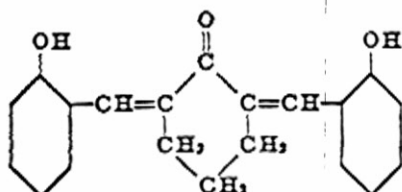
3-phenyl-5-(o-hydroxybenzal)-24-thiazolidione

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In the following compound Y and R together represent an aromatic ring:



2:6-disalicylaldehydicyclohexanone

These compounds may be substituted in the aromatic ring with groups including halide, nitro, amino, substituted amino, alkyl, aryl, and carboxyl groups. These groups may be substituted in the ring at any position except in most cases the position para with respect to the hydroxyl group. In certain cases, however, the substituted groups may occur both ortho and para to the hydroxyl group and in this case the coupling with the developer will occur in the position ortho with respect to the hydroxyl group.

As developing agents we contemplate using aromatic amino compounds which function as photographic developers. The compounds preferred for this purpose are para phenylenediamine and its substituted derivatives. These developers may be substituted in the amino groups as well as in the ring with alkyl, ester, or halide groups. The compounds which we prefer to use are dialkyl para phenylene diamines substituted in one amino group, the other amino group remaining unsubstituted. These compounds are ordinarily used in the salt form, such as the hydrochloride or sulfate, since these compounds are more stable than the amines themselves. Developing agents which may be used include diethyl para phenylenediamine, monomethyl para phenylenediamine hydrochloride and diethyl para phenylenediamine sulfate.

A developing formula which may be used is the following:

A	
Diethyl para phenylenediamine hydrochloride	1 gram
Sodium sulfite	0.5 gram
Sodium carbonate	20 grams
Water to	1 liter

B	
Coupler	1 gram
Acetone	50 cc

Add B to A.

The developing agent and the proportions of the ingredients used in the above formula may, of course, be varied. Solvents other than acetone, such as alcohols, may also be used.

The colors formed by the compounds of the present invention on coupling with the oxidation product of the developer in general range from blue to green. The colors of the specific dyes referred to above, as indicated by visual tests, are as follows:

Blue-green	1 - (o-hydroxycinnamyl) - benzothiazole
Blue-green	2 - (o - hydroxycinnamyl) pyridine
Blue-green	2 - (o - hydroxycinnamyl) thiazoline
Dark green	o-styrylphenol
Yellow-green	5-(o-hydroxybenzal)-2-thiohydantoin
Light green	3 - phenyl-5-(o-hydroxybenzal)-2:4-thiazolidione
Green	2:6-disalicylaldehydicyclohexanone

The color of dyes formed from compounds having substituent groups in the ring may vary according to the type of substituent group employed.

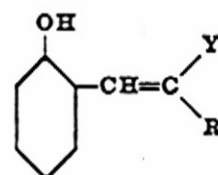
Although we have described our invention with particular reference to the use of the coupling compound in the developing solution itself, our invention is in no way limited to this method. As an alternative method, the coupler compound may be incorporated in the photographic layer before development, or before development and exposure. It may be adsorbed to the sensitive silver halide grain or chemically combined with the sensitive salt, or, in some cases, the silver salt of the coupler compound itself, without halide, may exhibit light sensitivity and coupling properties on development.

Our compounds may be used to form colored photographic images in films, plates, or paper when gelatin or other suitable colloid is used as the carrier for the silver halide constituting the sensitive salt. The emulsion treated to form the colored image may be on one or both sides of the support or in superposed layers on one or both sides of the support. Where two or more layers are used they may be differently sensitized to form natural colored images on development, according to the process described in application, Serial No. 8,516, filed February 27, 1935 by L. D. Mannes and L. Godowsky, Jr.

What we claim is:

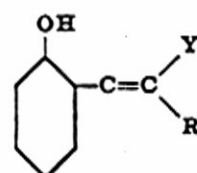
1. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and an ortho hydroxy styrene coupler compound containing a substituent group in the β position of the chain, with which the developing compound is capable of reacting on development.

2. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and a coupler compound having the formula



where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

3. A color-forming photographic developer comprising diethyl paraphenylenediamine hydrochloride and a coupler compound having the formula



where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen

atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

4. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and 2:6-disalicylaldehydohexanone.

5. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and an ortho hydroxystyrene compound having a heterocyclic-ring substituent in the β position of the chain.

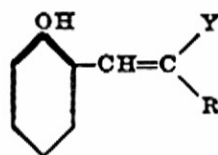
6. A color-forming photographic developer comprising an aromatic amino developing compound containing a primary amino group and 1-(o-hydroxycinnamyl)-benzothiazole.

7. A color-forming photographic developer comprising diethyl paraphenylenediamine hydrochloride and 2:6-disalicylaldehydohexanone.

8. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing compound containing a primary amino group with an ortho hydroxy styrene containing a substituent group in the β position of the chain.

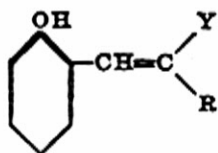
9. A photographic image comprising a dye formed by the coupling of the oxidation product of an aromatic amino developing compound containing a primary amino group with an ortho hydroxy styrene containing a substituent group in the β position of the chain.

10. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing compound containing a primary amino group with a compound having the formula



where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

11. A photographic image comprising a dye formed by the coupling of the development product of diethyl paraphenylenediamine hydrochloride with a compound having the formula

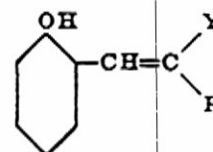


where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

12. The method of producing a colored photographic image in a gelatino-silver halide emul-

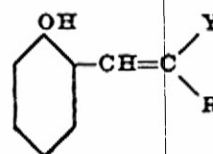
sion layer which comprises coupling the development product of an aromatic amino developing compound containing a primary amino group with an ortho hydroxy styrene containing a substituent group in the β position of the chain.

13. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer which comprises coupling the development product of an aromatic amino developing compound containing a primary amino group with a compound having the formula



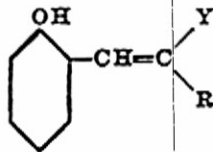
where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

14. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer which comprises coupling the development product of an aromatic amino developing compound containing a primary amino group with a compound present in the developer having the formula



where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

15. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer which comprises coupling the development product of an aromatic amino developing compound containing a primary amino group with a compound present in the emulsion layer having the formula



where Y—C—R is a structure selected from the class consisting of structures wherein Y—C—R together represent the atoms necessary to complete an organic ring selected from the class consisting of heterocyclic rings and carbocyclic rings, and structures wherein Y represents a hydrogen atom and R represents an organic ring selected from the class consisting of heterocyclic rings and aromatic rings.

LEOPOLD D. MANNES.
LEOPOLD GODOWSKY, Jr.
WILLARD D. PETERSON.

Evidence on Behalf of the Defendant

Mr. Reynolds: I should like to offer our exhibit in evidence, your Honor.

The Court: Yes, that may be admitted.

(Patent Office file was marked Defendant's Exhibit No. 1 and received in evidence.)

(Defendant's exhibit contains the following documents:)

A—Fischer U. S. Patent 1,102,028

B—Examiner's Statement

C—Supplemental Examiner's Statement

D—Decision of the Board of Appeals

UNITED STATES PATENT OFFICE.

RUDOLF FISCHER, OF STEGLITZ, NEAR BERLIN, GERMANY.

PROCESS OF MAKING COLORED PHOTOGRAPHS.

1,102,028.

Specification of Letters Patent.

Patented June 30, 1914.

No Drawing.

Application filed January 27, 1913. Serial No. 744,386.

To all whom it may concern:

Be it known that I, RUDOLF FISCHER, a citizen of the German Empire, and resident of Steglitz, near Berlin, Germany, have invented a certain new and useful Improved Process of Making Colored Photographs, of which the following is a specification.

The subject-matter of my invention is an improved process of making photographic pictures.

The development of photographic halogen-silver films leads, in general, to a black picture substantially composed of silver. Individual cases, are however, well known in which colored pictures can be obtained directly when developing. Thus, developing with pyrogallol yields a yellowish-brown picture, with indoxyl a blue, and with thioindoxyl a red picture. Also, the other customary photographic developers yield, under suitable conditions, *e. g.* absence of sodium sulfite and similar bodies, more or less colored pictures. The colors thus obtained are, however, either not very decided, or, as in the case of the developers from the indigo group, not readily obtainable.

Now I have found that exceedingly highly colored pictures can be very readily obtained by not using the oxidation products of the developers alone, but by adding to the developers substances which become coupled with those oxidation products of the developer which are formed while developing, and form colored bodies soluble with difficulty. According to the developers or coupling bodies which are employed I obtain representatives of various classes of coloring materials or dyes, of which the following are given as examples:—

p-amidophenols+phenols: indophenols,
p-phenylenediamins+phenols: indoanilins and oxazins,
p-phenylenediamins+amins: indamins,
p-phenylenediamins+thiophenols: indothio-phenols,

p-amidophenols
p-phenylenediamins } + { combinations containing acid methylene groups: azomethin.

The bodies soluble with most difficulty are obtained with p-phenylenediamin as developer and phenols or compounds with acid methylene groups as coupling bodies.

The p-phenylenediamins comprise the side chains homologues and core homologues,

also the substitutes of p-phenylenediamin in the amido group or in the core.

Examples:—p-phenylenediamin, p-toluylenediamin, amido-p-phenylenediamin, chlor-p-phenylenediamin, monoethyl-p-phenylenediamin, dimethyl-p-phenylenediamin. Further, the amido group may be included in a ring system: p-aminophenylene-piperidin.

By phenols, likewise, the side chains and core homologues and the substitution products are to be understood.

Example: phenol, cresol, naphthol, o-amidophenol, trichlor-naphthol, resorcin-methyl-ether, naphthol-sulfonic acid.

The acid methylene compounds may be both of an aliphatic and also of an aromatic nature.

Examples: ethyl-aceto-acetate, malononitrile, chloraceto-phenone, diketohydrindene, nitrobenzyl-cyanid, thioindoxyl.

Further, the methylene group may be substituted when the substitute is split during the reaction.

Examples: chlor-ethyl-aceto-acetate, thioindoxyl-carboxylic acid.

The coloring matter or dye produced in these processes of development can be reduced to leuco compounds which likewise possess developing properties and likewise yield colored pictures directly during the developing process when the oxidation products are soluble with difficulty. Here also it is found that the above specially mentioned classes of coloring materials yield the best results. The developing properties of a part of these classes are already known; for example, the developer pyramidol *i. e.* dioxydiphenylamin is a leuco-indophenol. Nevertheless, only black pictures were obtained, and it was not observed that colored oxidation products soluble with such difficulty could be obtained that colored pictures were obtained. It is preferable to omit the admixture of sodium sulfite or similar bodies. The employment of the leuco bodies is, however, not very preferable because they change readily, while the first described separate form of employment has the advantage that the components can be preserved separately and need be mixed only immediately before the development or when developing.

The colored developers can also be employed in such a form that they are incorporated in the film or the film-carrier, or a separate layer is applied to the layer or film

sensitive to light. Either the leuco compounds, the separate components, or only one of the two may be used. The coloring-material picture can be isolated by removing the silver by means of one of the well-known agents which will lighten the picture.

Examples.

1. 2 g. trichloronaphthol dissolved in 20 c. cms. acetone and added to the following solution:—2 g. hydrochlorid of p-phenylenediamin, 30 g. soda, 1000 cms. water. A greenish-blue picture is obtained.

2. 2 g. thymol dissolved in 20 cms. acetone are added to the following solution:—hydrochlorid of p-amidophenylenepiperidin, 40 g. soda, 100 cms. water. Blue picture.

3. 2 g. α -naphthol dissolved in 20 cms. acetone are added to the following solution:—2 g. hydrochlorid of dimethylparaphenylenediamin, 30 g. soda, 1000 cms. water. Blue picture.

4. 2 g. thioindoxyl-carboxylic acid dissolved in 40 c. cms. acetone are added to the following solution and shaken well:—2 g. hydrochlorid of monoethylparaphenylenediamin, 40 g. potash, 1000 cms. water. Red picture.

5. 2 g. o-nitrobenzylcyanid in 20 c. cms. acetone are added to a solution of 2 g. hydrochlorid of dimethyl paraphenylenediamin 30 g. soda, 1000 cms. water. Brownish-red picture.

6. 2 g. α -chlor-ethyl-aceto-acetate in 20 c. cms. acetone are added to 2 g. diethylparaphenylenediamin, 40 g. potash, 1000 cms. water. Yellow picture.

7. 2 g. p-nitrobenzylcyanid in 20 c. cms. acetone are added to 1 g. p-amidophenol, 40 g. potash, 1000 cms. water. Brown picture.

8. 2 g. 4-oxy-2 amido-4'diethylamido-diphenylamin, 50 g. potash, 1000 cms. water. Blue picture.

9. 2 g. 4-dimethylamidophenyl- μ -cyan-azomethin-phenyl. 100 g. potash, 100 cms. water. Orange-colored picture.

I claim:—

1. A process of making colored, photographic pictures, consisting in developing pictures on halogen-silver films with a developer that contains a substance which in connection with the oxidation product of the developer forms a colored body soluble with difficulty.

2. A process of making colored, photographic pictures, consisting in developing pictures on halogen-silver films with the leuco compounds of a product resulting from the connection of a developer with a substance which in connection with the oxidation product of such developer forms a colored body soluble with difficulty.

3. A process of making colored, photographic pictures, consisting in developing pictures on halogen-silver films with a developer and a substance which in connection with the oxidation product of the developer forms a colored body soluble with difficulty, the substances giving the color being placed in the layer to be developed, substantially as described.

4. A process of making colored, photographic pictures, consisting in developing pictures on halogen-silver films by aromatic diamins and aromatic hydroxyls.

5. A process of making colored, photographic pictures, consisting in developing pictures on halogen-silver films by aromatic diamins and compounds containing methylene groups of an acid character.

In testimony whereof, I affix my signature in the presence of two witnesses.

RUDOLF FISCHER.

Witnesses:

WOLDEMAR HAUPT,
HENRY HASPER.

Deft. Ex. No. 1-B

Mailed May 31, 1940

FK:hw

Paper #9

DEPARTMENT OF COMMERCE
U. S. Patent Office
Washington, D. C.

In re application of	} On Appeal Before the Board of Appeals.
K. Schinzel	
Serial No. 263,945	
Filed March 24, 1939	
Fro: Phenolic and Naphtholic Couplers Containing Sulfonamide Groups.	

Examiner's Statement.

This is an appeal from the action of the examiner finally rejecting claims 7 to 12 inclusive (claims 1 to 6 and 15 to 18 have been allowed and claims 13 and 14 are now believed allowable in view of the amendment of Feb. 20, 1940).

The appealed claims are:

7. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

8. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

9. A photographic image comprising a dye formed by the coupling of the development product of a paraphenylenediamine developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

10. A photographic image comprising a dye formed by the coupling of the development product of a paraphenylenediamine developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

11. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-8-sulfonamide.

12. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-3:6-disulfonamide.

The reference relied on is:

Fischer 1,102,028

June 30, 1914.

Applicant's invention is drawn to color photography and relates more specifically to a novel color-coupler for use in colour photography. In a well known process for producing color images from an exposed silver halide emulsion, the emulsion is developed with a primary aromatic amino developing agent in the presence of a compound, called a color "coupler", which reacts with the oxidation product of the developer and produces a colour image in situ with the developed silver image.

Applicant has disclosed a new coupler and has been allowed claims to a developer containing this coupler and to a method of producing a colored image by developing an exposed silver

halide emulsion with a primary aromatic amino developing agent in the presence of this coupler.

The appealed claims are drawn to a photographic image comprising a dye formed by the reaction of the oxidation product of a developer and the coupler. They were rejected as being drawn to an old combination as evidenced by Fischer and also as failing to define applicant's invention.

Fischer discloses the same process as is shown by the applicant, but uses different couplers. It is not seen that the substitution of a different coupler with a consequent change in the chemical composition of the dye produced, changes the relation between the gelatine and the resultant dye image. In both cases there will be a layer of gelatin having varying densities of dye in accordance with the variation in the image. The claim is accordingly believed drawn to an old combination as evidenced by Fischer.

Applicant has submitted an affidavit showing that his dyes are more intense and of a better shade of blue than the dyes produced by the most analogous compound disclosed in Fischer. The difference is, however, merely one of degree and is not believed sufficient to avoid the rejection.

The claims were further rejected as failing to define applicant's invention. They are broad enough to read on a process in which the development product is produced at one point during the ordinary development of a black and white image and then coupled at an entirely independent point with the coupler to produce a dye which may then be used to print a photographic image in an ordinary printing press. This is obviously outside the scope of applicant's disclosure which is limited to the process in which the development and color production occur simultaneously.

Furthermore, since the introductory phrase is not a limiting one, applicant is merely claiming a dye produced in a certain manner which likewise fails to point out applicant's invention.

For the reasons advanced above, it is believed that the rejection was proper and the examiner should be affirmed.

Respectfully,
Examiner,
Division 7.

Attorney:
Newton M. Perrins
c/o Eastman Kodak Company
343 State Street
Rochester, New York.

Deft. Ex. No. 1-C

Division 7
Room 5725
FK/VS

Paper #13

DEPARTMENT OF COMMERCE

U. S. Patent Office
Washington.

Mailed November 20, 1940

Supplemental Examiner's Statement.

In re application of
Karl Schinzel
Serial No. 263,945
Filed March 24, 1939

For: Phenolic and Naphtholic
Couplers Containing
Sulfonamide Groups.

} Before the Board of Appeals.

This application has been remanded to the Examiner for consideration of an affidavit filed under the provisions of Rule 76.

This affidavit is similar to the affidavit submitted on February 21, 1940, and shows that the transmission curve of the dye produced by a coupler in the class of couplers disclosed by applicant is different from that of an analogous compound in Fischer. It is possible from purely theoretical considerations to draw transmission curves which would give perfect color reproduction and it would be obviously desirable to use couplers which produced dyes most nearly approaching this theoretically perfect color. Applicant has discovered a coupler which, as indicated in both affidavits, produces a dye having more desirable transmission characteristics than the dyes produced by Fischer and the claims directed to this coupler have been allowed. The finished print, however, differs only in that the dye has a slightly different color from that of the Fischer print and such difference is believed insufficient to warrant the allowance of claims directed to the print. The selection of a dye having desirable transmission characteristics is of itself not believed to constitute invention; the invention being rather in the method used to deposit the dye in image form.

The pioneer patent to Fischer from which applicant has selected his compounds for comparison was cited merely to indicate that the process of color development was old and is one out of approximately fifty patents directed to the process of color development which have been granted since the issuance of this patent. Many compounds other than those disclosed in Fischer have been disclosed in the art and successfully used in practice particularly in the "Kodachrome" process of the assignee of the applicant. Applicant's coupler produces a print having a more nearly perfect color but the invention is believed exhausted and completely protected by the claims which have been allowed to the coupler.

For the reasons advanced above the affidavit submitted under Rule 76 is considered insufficient to overcome the rejection and

it is believed that the final rejection was proper and the Examiner should be affirmed.

Acting Examiner.

Deft. Ex. No. 1-D

Appeal No. 35,323

OB

Hearing:

November 7, 1940

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Ex parte Karl Schinzel

Application for Patent filed March 24, 1939, Serial No. 263,945. Phenolic and Naphtholic Couplers Containing Sulfonamide Groups.

Messrs. Newton M. Perrins & R. Frank Smith for applicant.

This is an appeal from the action of the Primary Examiner finally rejecting claims 7 to 12, inclusive.

Claim 7 is illustrative and reads as follows:

7. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.

The reference relied upon is:

Fischer

1,102,028

June 30, 1914

Appellant has presented a novel color coupler for use in color photography. The examiner states:

"In a well known process for producing color images from an exposed silver halide emulsion, the emulsion is developed with a primary aromatic amino developing agent in the presence of a compound, called a color 'coupler', which reacts with the oxidation product of the developer and produces a colour image in situ with the developed silver image."

The examiner has allowed claims to the new coupler and also allowed claims to the method of producing a colored image by developing an exposed silver halide emulsion with a primary aromatic amino developing agent in the presence of this coupler. The claims on appeal are drawn to a photographic image comprising a dye formed by the reaction of the oxidation product of a developer and a coupler.

The patent to Fischer discloses the same process but uses different couplers. The examiner states that by the use of a different coupler and consequent change in the chemical composition of the dye produced, there is no change in the relation between the gelatin and the resultant dye image. There will be a layer of gelatin having varying densities of dye in accordance with the variation of the image. Appellant urges that his dyes are more intense and of a better shade of blue than the dyes produced by the most analogous compound disclosed by Fischer. As to this the examiner holds that the difference is merely one of degree and not believed sufficient to avoid the rejection.

As the examiner stated, the selection of a dye having desirable transmission characteristics is of itself not believed to constitute invention but the invention resides rather in the method used to deposit the dye in image form.

It seems to us appellant has obtained suitable protection for his invention by the allowance of claims to the color coupler and also claims to the method of producing a colored photographic image. As far as the photographic image itself is concerned, it differs from the photographic image of the prior art as stated by the examiner merely in a difference of degree

which may be of advantage, but the invention is properly expressed in the allowed claims. We believe the examiner's holding should be sustained.

The claims are further rejected as failing to define applicant's invention for certain reasons given by the examiner. These claims call for a dye produced in a certain manner if the introductory phrase is ignored and even if the introductory phrase were included, it would broadly cover the production of an image by the application of a dye and we believe the examiner is warranted in his holding. If the claims were amended as suggested, they would cover the same invention as defined in the process claims, only differing in expression.

The decision of the examiner is affirmed.

December 3, 1940
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Examiner-in-Chief
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BOARD
OF
APPEALS

BRIEF FOR APPELLANT

IN THE
United States Court of Appeals
FOR THE DISTRICT OF COLUMBIA

Appeal No. 8406

EASTMAN KODAK COMPANY,

Appellant.

vs.

CONWAY P. COE, Commissioner of Patents,

Appellee.

**APPEAL FROM THE JUDGMENT OF THE
DISTRICT COURT OF THE UNITED STATES
FOR THE DISTRICT OF COLUMBIA**

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IN THE
United States Court of Appeals
FOR THE DISTRICT OF COLUMBIA

Appeal No. 8406

EASTMAN KODAK COMPANY

Appellant,

vs.

CONWAY P. COE, Commissioner of Patents,

Appellee.

BRIEF FOR APPELLANT

This is an appeal from the Final Judgment (dated October 27, 1942) of the United States District Court for the District of Columbia (Appellant's App. 6) dismissing Appellant's Bill of Complaint which sought the grant of United States Letters Patent containing claims 7, 8, 9, 10, 11 and 12 (Appellant's App. 1) of Schinzel Application Serial No. 263,945 (Appellant's App. 27).

JURISDICTIONAL STATEMENT

The U. S. District Court for the District of Columbia obtained jurisdiction of this case by virtue of Section 4915 of the Revised Statutes (U. S. C. Title 35, Section 63) under which Appellant's Bill of Complaint (Appellant's App. 1) was filed on May 29, 1941.

This Honorable Court of Appeals has jurisdiction of this Appeal under the Act of February 9, 1893, c. 74, 27 Stat. 434, as amended, and as incorporated in the Code of the District of Columbia, (1940) Title 17, Sec. 101, the appeal being properly docketed and prosecuted according to the Rules of this Court.

STATEMENT OF CASE

After due proceedings in the U. S. Patent Office, in which the Board of Appeals rejected (Appellant's App. 69), claims 7 to 12, inclusive (Appellant's App. 2, 3, 32 and 33), of Schinzel Application Serial No. 263,945 (Appellant's App. 27), Appellant, as assignee of said Schinzel Application, filed its Bill of Complaint (Appellant's App. 1) against the Commissioner of Patents alleging his refusal to grant Letters Patent containing claims 7 to 12, which are directed to a photographic image comprising a dye formed from a specified coupler compound. The Commissioner duly answered, alleging said claims 7 to 12 to be unpatentable over a single prior art patent disclosing a photographic image different from that recited in said claims 7 to 12.

Full trial was had in due course, at which Plaintiff took the testimony of two witnesses (Appellant's App. 6 to 25), showing the inadequacy of the prior art patent relied upon, the utility of the couplers used in the preparation of the dye image, and the practical success of the photographic image covered by the claims. The inventor, being a former resident of Czechoslovakia, and now believed to be in Germany, was unable to testify in his own behalf.

The Solicitor for the Commissioner cross-examined one of Plaintiff's witnesses, but produced no witness in his own behalf. The single prior art patent relied upon by the Commissioner was the subject of extensive investigation about which the witnesses testified. Four additional patents were introduced by the Plaintiff at the trial (Appellant's App. 25) to illustrate the type of claims which the Patent Office customarily allows. Two of these patents will be referred to later; the other two are less pertinent and will be ignored here in the interest of brevity.

STATUTES

The pertinent statutes upon which the decision of this case depends are as follows:

Sec. 4886. R. S. (U. S. C., title 35, sec. 31). Any person who has invented or discovered any new and useful art, machine, manufacture, or composition of matter, or any new and useful improvements thereof, * * * not known or used by others in this country, before his invention or discovery thereof, and not patented or described in any printed publication in this or any foreign country, before his invention or discovery thereof * * * may, upon payment of the fees required by law, and other due proceeding had, obtain a patent therefor.

Sec. 4915. R. S. (U. S. C., title 35, sec. 63). Whenever a patent on application is refused by the Board of Appeals * * * the applicant, * * * may have remedy by bill in equity, if filed within six months after such refusal or decision; and the court having cognizance thereof, on notice to adverse parties and other due proceedings had, may adjudge that such applicant is entitled, according to law, to receive a patent for his invention, as specified in his claim or for any part thereof, as the facts in the case may appear. * * *

Code of the District of Columbia (1940) Tit. 17, Sec. 101. Any party aggrieved by any final order, judgment, or decree of the District Court of the United States for the District of Columbia, or of any justice thereof, may appeal therefrom to the said United States Court of Appeals for the District of Columbia; and upon such appeal, the United States Court of Appeals for the District of Columbia shall review such order, judgment, or decree, and affirm, reverse, or modify the same as shall be just, * * *.

STATEMENT OF POINTS

1. There was error in the implicit finding of the third Finding of Fact, namely, that the rejected claims are unpatentable over the allowed claims. Allowed claims should not be made a measure of the patentability of rejected claims. The third Finding of Fact is as follows:

"Claims have been allowed in the Schinzel application to a developer comprising an aromatic amino developing agent and the particular coupler compound disclosed, and claims have also been allowed to the method of producing images by the use of this developer and a silver halide emulsion. The claims involved in the present action are drawn to an image comprising a dye formed by the use of the same coupler and developing agent which are recited in the allowed claims."

2. The fourth Finding of Fact is not in accordance with the evidence since the product of the claims differs from the product of the prior art in color and in the amount which can be produced in a photographic layer. The fourth Finding of Fact is as follows:

"The patent to Fischer, No. 1,102,028, discloses a process of making colored images, which differs from that of the Schinzel application only in the specific coupler compound used."

3. There was error in the fifth Finding of Fact, since the coupler compound of Schinzel is not used in the same manner as the coupler compound of Fischer. The fifth Finding of Fact is as follows:

"The only novel element of the claims here involved is the coupler compound, which compound is used in exactly the same manner as the corresponding coupler compound of the Fischer patent."

4. There was error in the sixth Finding of Fact, which is as follows:

"The claims here involved are drawn to an old combination of a coupler compound and a developing agent to form a photographic image, and are, therefore, unpatentable."

SUMMARY OF ARGUMENT

1. The claims are drawn to subject matter on which United States Letters Patent may be properly granted.

2. Allowed claims should not be made a measure of the patentability of rejected claims.

3. The Commissioner's evidence.

The Fischer patent discloses only one workable example and that one cannot be used commercially.

4. The Plaintiff's evidence.

A. The color of plaintiff's dyes is better for purposes of color photography than the color of the single prior art dyes.

B. The Fischer dye contains no sulfonamide group or sulfonic acid group.

C. The Fischer dye is not operative in a commercial process.

D. The sulfonamide coupler of Schinzel produces a dye image suitable for commercial use and of the correct color.

5. The claims are not drawn to an "old combination".

6. The form of the claims is proper.

ARGUMENT

Subject Matter of Claims

Natural color photography depends on the ability of sensitive photographic material to record separately the three primary colors—red, green and blue—since combinations of these colors can reproduce nearly all of the hues present in nature. The most efficient method of recording these colors in photographic material is to use the "subtractive" process, in which the image formed by red light is represented by the complementary color blue-green or cyan, the image formed by green light is represented by the complementary color magenta, and the image formed by blue light is represented by the complementary color yellow.

A convenient way of producing these complementary colors in photographic material is to allow the photographic developing agent to react on development with a compound known as a "coupler". This reaction produces a dye wherever the

photographic layer has been exposed and, therefore, forms a dye image.

Schinzel, the applicant, discovered that blue-green dyes for color photography could be produced by using as a coupler a phenol or a naphthol containing a sulfonamide group. (Formula, Appellant's App. 35, Ex. 2). Claims 13 and 14 of the application, drawn to this process, have been allowed. Claims 1 to 6, drawn to a photographic developing solution containing a developing agent and the sulfonamide coupler have also been allowed. By the allowance of these claims, the Patent Office has admitted the existence of patentable merit in Schinzel's discovery.

A part of Schinzel's invention was the discovery that a novel photographic dye image could be produced from the sulfonamide couplers used in his process. These claims, which were the only ones involved in the Civil Action below and in this appeal, are as follows:

7. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.
8. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.
9. A photographic image comprising a dye formed by the coupling of the development product of a para-phenylene-diamine developing agent containing a primary amino group with a coupler compound selected from the group consisting of phenols and naphthols containing at least one sulfonamide group.
10. A photographic image comprising a dye formed by the coupling of the development product of a para-phenylene-diamine developing agent containing a primary amino group with a coupler compound comprising an α -naphthol containing at least one sulfonamide group.

11. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-8-sulfonamide.

12. A photographic image comprising a dye formed by the coupling of the development product of an aromatic amino developing agent containing a primary amino group with a coupler compound comprising α -naphthol-3:6-disulfonamide.

The novel feature of these claims is *the image* comprising or composed of the dye made by coupling the development product of the developing agent with the phenol or naphthol containing a sulfonamide group. This image is a proper subject for United States Letters Patent. Section 4886 of the Revised Statutes provides for patents on *manufactures*. The term "manufacture", according to *Johnson et al v. Johnston*, 60 Fed. 618 (1894), a decision of the United States Circuit Court in the Third Circuit,

"as used in the patent law has a very comprehensive sense, embracing whatever is made by the art or industry of man not being a machine, a composition of matter, or a design."

The photographic image of the claims is not something which exists only in the mind's eye but is a visible, tangible object which can be examined and reproduced. It is a true "manufacture" within the sense of Section 4886 of the Revised Statutes.

Allowed Claims Immaterial

Although one prior art patent was cited against the Schinzel application, the principal basis upon which the product claims in issue here were refused appears to be that the scope of Schinzel's protection has been exhausted by allowance of the method claims and claims to the developing solution. The Patent Office Board of Appeals said:

"As far as the photographic image itself is concerned, it differs from the photographic image of the prior art

as stated by the Examiner merely in a difference of degree which may be of advantage, *but the invention is properly expressed in the allowed claims.*" (Italics ours.) (Appellant's App. 70.)

The third Finding of Fact also implies that the claims are unpatentable because claims drawn to the developing solution and to the method of producing images have been allowed. The third Finding of Fact concludes with the statement that

"The claims involved in the present action are drawn to an image comprising a dye formed by the use of the same coupler and developing agent which are recited in the allowed claims."

While it does not specifically so state, the third Finding of Fact contains the definite implication that the claims involved in the present action should not be allowed because other claims of different scope have been allowed in the same application. The implicit finding contained in this statement is believed to be erroneous in law and is one of the points upon which the present appeal is based.

The effect of this position of the Patent Office and of the District Court below is to make the allowed claims a criterion for the patentability of the rejected claims. This is believed to be incorrect practice since allowed claims, in general, should not be made a measure of the patentability of rejected claims. The prior art is the only true mixture of the patentability of the claims. The Board of Appeals itself has said that allowed claims should not be made a measure of patentability of other claims in the same application. In *Ex parte Frank et al*, 39 U. S. Patents Quarterly 526, the Board of Appeals ruled that a rejection on prior art and also on an allowed claim was improper. An effective rejection of this type has been made in the present case and approved by the District Court in its third Finding of Fact by holding that the invention is properly expressed in the allowed claims.

This court has recently stated, in *Sharp v. Coe*, — App. D. C. — ; 125 F. (2d) 185, that allowed claims should not be

made a conclusive measure of the patentability of rejected claims. The following statement is quoted from the opinion in that case:

"In respect of the question whether the allowed claims may be used as a measure of the patentability of the rejected claims: We are in agreement that the action of the Commissioner on allowed claims is not to be taken as a conclusive measure of the patentability of rejected claims. Patentability of the latter must be determined ultimately by comparison with the prior art."

The opinion in *Sharp v. Coe* stated that the action of the Commissioner on allowed claims could be taken into consideration in determining the patentability of rejected claims; nevertheless, that the patentability of the latter *must be determined ultimately by comparison with the prior art*.

While the process claims and the developer claims which have been allowed afford the applicant protection for the process which he has invented, they do not give him adequate protection where the product is made abroad and imported to this country. It is true that some protection is afforded by the Tariff Laws relating to the importation of a product made abroad by a process patented in the United States, but this remedy is not entirely satisfactory. Where a product made abroad has entered the United States there can be no injunction to prevent its sale nor can damages for infringement be awarded. A process patent is not infringed by sale of the product (*Merrill v. Yeomans*, 94 U. S. 568). If suit for infringement were brought in a jurisdiction where the product was sold, there could be no recovery unless the product was made in that jurisdiction by the process of the patent.

The Supreme Court has held that a patentee who has invented a new process whereby a new article of manufacture is produced may separately claim both the art and the manufacture—that is, both the process and the product. (*Merrill v. Yeomans*, 94 U. S. 568). If the article or product is new, it may be patented just as the new process may be patented. In

the present case, therefore, the fact that process claims have been allowed is not a sufficient reason for denying applicant claims to the product if such product is otherwise novel and patentable.

The Commissioner's Evidence

The single prior art patent cited by the Patent Office, the Fischer patent 1,102,028, discloses a color development process of the same general type as that of the Schinzel application. The same developing agents are used but the couplers differ. The portion of the Fischer patent which is alleged to be pertinent to the present claims is the passage on page 1, line 70 that "naphthol-sulfonic acid" can be used as a coupler. While the Fischer patent does not describe any specific naphthol sulfonic acid, several of them were selected by witnesses for the plaintiff for comparison with the sulfonamide couplers of Schinzel (Appellant's App. 9). The findings of the expert witnesses with respect to these compounds will be dealt with more fully below in discussing the plaintiff's evidence. The Board of Appeals, as the following statement from their decision shows, (Appellant's App. 70) took the position that the photographic image of the Schinzel claims differed from the prior art only in degree and that the invention was properly expressed in the allowed claims:

"As far as the photographic image itself is concerned, it differs from the photographic image of the prior art as stated by the Examiner merely in a difference of degree which may be of advantage but the invention is properly expressed in the allowed claims."

When expressing this opinion that applicant's product differed from the prior art only in degree, the Board of Appeals had before it only the evidence presented in the Patent Office that the Schinzel dyes had improved light absorption characteristics for purposes of color photography when compared with the single dye which could be produced by use of the Fischer couplers. New evidence presented in the District Court showed the difference to be one of *kind* and not of

degree only. In addition to the improvement in light absorption characteristics brought about by the introduction of a sulfonamide group into the couplers, the Schinzel dyes were also shown to be suitable for purposes of natural color photography whereas the single dye which could be produced by use of the Fischer coupler was totally useless for this purpose.

The Solicitor for the Commissioner brought out on cross-examination of plaintiff's witness Vittum that the improvement afforded by the Schinzel invention over that of Fischer was in the specific dye. The following examination of the witness took place (Appellant's App. 22) :

"By Mr. Reynolds:

Q. Now, isn't it true that the only difference between the Schinzel invention and that of Fischer resides in the specific dye that is used in the two cases?

A. Yes, it is.

Q. That is, the actual steps of using the dye to make a photographic image are the same in each case, are they not?

A. Yes.

Q. So that any superiority that Schinzel's picture would have over Fischer's is due solely to the particular dye that is used; isn't that true?

A. Yes.

Since the photographic image comprising or composed of the dye is the product claimed and since it was brought out on cross-examination that the dye was a novel element of the claim, it appears that the Solicitor for the Commissioner has demonstrated the exact point for which the appellant is contending, that is, that the dye image product is a novel and patentable object.

The Plaintiff's Evidence

In discussing the plaintiff's evidence, we fully appreciate the fact that in view of such decisions by this Court as *Abbott v. Coe*, 71 Appeals D. C. 195; 109 Fed. (2d) 449, appellant's burden is to convince this court, not that the evidence supports a finding of invention, but that the District Court's finding that there was none is not consistent with the evidence.

Plaintiff's evidence shows that the color of the dye image defined by the claims is better for color photography than the color of the prior art dye. One purpose of the present invention is to provide dyes having desirable transmission characteristics for multi-color photography (Schinzel application, Appellant's App. 27). Any improvement in this direction brought about by the use of a special class of chemical compounds is indicative of invention.

In order to compare the dye obtained from the Fischer coupler with dyes obtained from the couplers of the Schinzel application, eight examples of the Schinzel couplers were prepared and dye images made from them for comparison with the Fischer dye. These dye images, plaintiff's Exhibit 6-A, were used in the preparation of graphs in which the intensity of the dye is represented by the height of the maximum curve and the light absorption properties are represented by the position of the curve, that is, a dye absorbing more red light is represented by a curve shifted toward the right. (Testimony of Vittum, Appellant's App. 11). These graphs were transferred to a single sheet, plaintiff's exhibit 6-J, (Appellant's App. 48) to form a composite record of the results. The dye strips from which these curves were obtained were prepared in such a way that the dye densities were substantially equal, that is, the maxima of the curves were made to correspond (Testimony of Vittum, Appellant's App. 11).

It will be noted that in nearly every case, particularly in the case of the graphs numbered 2, 3, 4, 6, 7 and 8 the solid

line curve representing the Schinzel dyes is shifted toward the right, indicating increased red light absorption, which is a desirable property of the blue-green dye for multi-color photography. Vittum testified as follows with respect to these curves (Appellant's App. 12) :

Q. Dr. Vittum, will you refer to these curves and explain what the dotted curves are?

A. Each one of these curves contains two separate curves, a dotted curve and a solid-line curve. The dotted curve, as you will see, is identical in all the diagrams, and that represents the one Fischer dye image that we were able to obtain, namely, the dye from 1-naphthol-4-sulfonic acid. The solid line curves represent the various Schinzel dyes, each of which contains the sulfonamide linkage.

Q. What comparison do these curves show between the Schinzel dyes and the Fischer dye?

A. These curves show that the majority of the Schinzel couplers are superior in their light-absorbing characteristic to the Fischer dye.

Q. What region on those charts should theoretically be absorbed for purposes of natural-color photography?

A. For natural-color photography the ideal cyan dye would be one that absorbs completely the red end of the spectrum, namely, that represented on these diagrams as falling between 600 and 700. The theoretical dye should also absorb none of the blue region—that is, from 400 to 500—nor the green region, which is from 500 to 600.

Q. And are the Schinzel dyes better with respect to red light absorption than the Fischer dye?

A. Yes, in nearly every case one can see a definite advantage with respect to red absorption for the Schinzel dyes.

With the Schinzel dyes, all of which contain a sulfonamide group, there is a definite shift in light absorption toward the red end of the spectrum and a consequent improvement in the value of the dye for multi-color photography. This improvement is brought about by the substitution of a definite

chemical group—the sulfonamide group—in the dye intermediates, which results in improved dye colors.

As mentioned previously, except for one example, the Fischer couplers are inoperative to produce any dye image whatsoever in a photographic layer. The witness Vittum referred to the disclosure of the Fischer patent as follows (Appellant's App. 8):

"A. The couplers mentioned by Fischer are not defined exactly. As I recall, the exact wording of the Fischer specification says "naphthol sulfonic acid," which could refer to a variety of arrangements of the groups within the molecule. For example, you have on this sheet the two compounds which would fall under the Fischer definition: "1-naphthol-4-sulfonic acid" and "1-naphthol-5-sulfonic acid". Both of these couplers are characterized by the presence in the molecule of the sulfonic acid, but that is the SO_2OH grouping. The Schinzel couplers, on the other hand, are characterized by the presence in the molecule of the substituent group SO_2NH , which is commonly referred to as a sulfonamide linkage."

In comparing the Fischer dyes with those of Schinzel, it was necessary to assume certain specific examples of the class mentioned in the Fischer patent, the examples being compounds which were commercially available (Vittum notebook, page 91, Appellant's App. 40).

According to Vittum's testimony, only one of the Fischer examples was operative (Appellant's App. 9):

"A. We found in those tests that of the sulfonic acid derivatives of alpha naphthol—that is, of the Fischer couplers—only one yielded a dye image at all. The others gave no dye image or no appreciable dye image. The Schinzel couplers, on the other hand, all yielded dye images appearing to have useful characteristics."

Vittum testified that the single operative example of Fischer formed a dye by loosing its sulfonic acid group during coupling (Appellant's App. 13):

"By Mr. Smith:

"Q. Then those tests showed that the single Fischer coupler which did produce a dye did so by reason of losing its sulfonic acid group during coupling; is that right?

A. That is right."

The witness Weissberger, also a competent organic chemist, conducted quantitative tests on the dye formed from the operative example of Fischer and testified as follows regarding it (Appellant's App. 25):

"Q. Was it your conclusion, then, from these tests that you made, that the dye from 1-naphthol-4-sulfonic acid disclosed in the Fischer patent contained no sulfur or sulfonic acid?

A. That is right."

This testimony with respect to the sulfonic acid group of the Fischer example indicates that no dye image was known containing a sulfonic acid group. In every case where a coupler containing a sulfonic acid group was used, as the compounds 9, 10 and 12 described on page 93 of the Vittum notebook (Appellant's App. 42), no dye image was produced. The worker in this art, in examining the Fischer disclosure would therefore be led to believe that a sulfonic acid group was undesirable in a color coupler, since no dye image could be produced from a coupler containing it. He would be led away from the use of a sulfonic acid group in a coupler, and similarly from the related sulfonamide group. The Fischer patent would teach that such groups were undesirable in couplers, whereas Schinzel found them to be highly desirable in couplers used in the production of photographic images. Where a patent disclosure *leads away from* rather than toward the disclosure of an application it cannot be said to constitute a teaching of the feature claimed in the application.

With respect to the commercial application of the dye image of the claims, the witness Vittum testified that the

Fischer dye was totally unsatisfactory and inoperative. Plaintiff's Exhibit 7 showed the results of an attempt to use the Fischer dyes in a commercial multi-layer film coating. A commercial multi-layer film contains three superposed emulsion layers each sensitive to one of the three primary colors. The red sensitive emulsion layer is ordinarily coated nearest the base or support of the film and the cyan or blue-green dye image is produced in this layer (Appellant's App. 16). The films of Exhibit 7 were of this type. This film was treated so that an image would be formed only in the lowermost layer in which a blue-green image should be produced. In the case of films 1 and 2, Exhibit 7, Schinzel-type couplers were used and in the case of films 3 and 4, Exhibit 7, Fischer couplers were employed. The specific couplers used are described on page 138 of the Vittum notebook, Exhibit 5C (Appellant's App. 45).

It is clearly evident from Exhibit 7 that satisfactory dye images were produced in the film when employing the Schinzel couplers, whereas totally unsatisfactory images were produced when employing the prior art Fischer couplers. In his record of the results of these tests, the witness Vittum (Notebook, pages 140-141, Exhibit 5C, Appellant's App. 47) explained why an image could be obtained with the Fischer coupler in the earlier tests illustrated (Exhibit 3B and Exhibit 6), while no image could be obtained using a commercial multi-layer material for which the Schinzel invention is intended. A thinner emulsion layer is used in a multi-layer material and in such material no dye could be obtained with the Fischer couplers. Vittum stated that the use of a thick emulsion layer such as those employed in the earlier test and a strong developer formula would be unsuitable for multi-layer material since

"Such conditions could not prevail in a practical multi-layer material" (Vittum Notebook, page 141, Exhibit 5C, Appellant's App. 47).

Vittum also testified as follows (Appellant's App. 19) that the film employed in these tests was regular commercial film:

"Q. Was this film that you used here regular commercial film?

A. Yes, this was regular Kodachrome 16 millimeter film."

In order to bring out the results of these tests in a more striking manner, they were repeated on print material which had three emulsion layers similar to those of the films of Exhibit 7, but in which the magenta and yellow dye images necessary to complete a natural color picture were also laid down in the superposed emulsion layers. These prints were received in evidence as Exhibit 8, print No. 1 employing a sulfonamide coupler of the Schinzel type, and prints 3 and 4 using sulfonic acid couplers of the Fischer class. Print No. 1 was made on a regular production machine with a regular production formula and is a satisfactory and pleasing natural color picture. Prints 3 and 4 were made in an identical manner except that naphthol sulfonic acids of the Fischer type were substituted for the sulfonamide coupler of Schinzel. Vittum testified, and it is also apparent from the pictures themselves, that no blue-green dye image is produced in the prints 3 and 4 (Appellant's App. 20). Vittum stated as follows:

"Q. What was the effect of using naphthol sulfonic acids on pictures 3 and 4 of this exhibit?

A. Well, we were unable to obtain a dye of the Fischer type in the bottom layer in anywhere near sufficient quantity to produce a satisfactory color photograph."

In these tests Vittum stated that he used in prints 3 and 4 *five times the coupler concentration* of cyan coupler that was used in the production of print No. 1. In spite of this great increase in coupler concentration in an effort to produce more blue-green dye in the layer using the Fischer couplers, no dye was produced with these couplers (Appellant's App. 21).

This testimony clearly showed that the sulfonamide group in the coupler was the important factor in the production of a usable photographic dye image. This was no mere isolated property of a single example, but was true of every one of the Schinzel couplers tested, as indicated by plaintiff's Exhibit 6J. All of the Schinzel couplers formed dye images. The sulfonamide couplers were suitable for commercial use, whereas the Fischer couplers were not. Schinzel's discovery of the employment of the sulfonamide group in the coupler was the factor that made the photographic dye image useful. This substitution of materials brings the invention within the scope of the following statement of the Supreme Court in *Hicks v. Kelsey*, 18 Wall. 670, 673, quoted with approval in the opinion of this Court in *Gasoline Products Corporation Inc. v. Coe*, (66 App. D. C. 333) :

"The use of one material instead of another in constructing a known machine is, in most cases, so obviously a matter of mere mechanical judgment, and not of invention, that it cannot be called an invention, unless some new and useful result, an increase of efficiency, or a decided saving in the operation, is clearly attained."

If Schinzel's dye is considered a new material used in place of the dye of Fischer, it satisfies all of the requirements for invention approved by this Court in *Gasoline Products Co. Inc. v. Coe*. The production of a usable multi-layer picture is assuredly *a new and useful result*. There is no evidence that any such picture had been made by the Fischer method prior to the present applicant's discovery, in spite of the length of time which elapsed between the date of the Fischer patent and the date of Schinzel's application. Applicant's dye effected a *great increase in efficiency*, since it was a commercial success using only one-fifth the amount of dye intermediate, or coupler, used to produce the Fischer dye, and even so, no appreciable dye was produced using the Fischer coupler. Even if a satisfactory dye image could have been produced with the Fischer dye in a multi-layer material, there would be a decided *saving in the operation* of color

development by use of the Schinzel dye. All of these factors are highly persuasive of the existence of a patentable invention.

The evidence for the plaintiff brought out, therefore, that

(a) Plaintiff's dye has better light absorption properties for color photography than Fischer's dye because of the presence of a sulfonamide group,

(b) Any Fischer coupler containing a sulfonic acid group forms no dye *by any development method*, so that the *teaching is away from* the use of the related sulfonamide group,

(c) The Fischer dye is not operative in a commercial multi-layer color process, for which applicant's dye is intended,

(d) The Schinzel dye contains a sulfonamide group and therefore is suitable for commercial use and has the correct color for color photography.

"Old Combination"

The sixth Finding of Fact states that the claims are drawn to an old combination of a *coupler compound* and a *developing agent* to form the photographic image and are, therefore, unpatentable (italics ours). The rule with respect to "old combinations", or unpatentable combination, of elements was laid down by the Supreme Court in *Loom Company v. Higgins*, 105 U. S. 580, 591 (1881), in the following words:

"It may be laid down as a general rule, though perhaps not an invariable one, that if a new combination and arrangement of known elements produce a new and beneficial result, never attained before, it is evidence of invention."

The most recent Supreme Court case dealing with old combinations is *Lincoln Engineering Company v. Stewart-Warner Company*, 303 U. S. 545, decided March 28, 1938. The *Lincoln* case was a suit for contributory infringement

in which respondent charged that the petitioner sold fittings of the type described in the respondent's patent and which were intended to be used with the gun and coupler of the patent. The claims of the patent were drawn to the combination of a headed nipple for receiving lubricant, a lubricant compressor having a coupling member * * *, a cylinder and a piston movable within the cylinder. The Supreme Court held that the invention, if any, was in the "coupling member" although no claims were drawn to this member as such. This case was relied upon by the Solicitor for the Commissioner in the District Court.

Two cases relating to old combination have been decided by this Court since the *Lincoln* case. In the first of these, *Electrons, Incorporated, et al. v. Coe*, 69 App. D. C. 181; 99 F. (2d) 414, the Court said that a combination of old elements may be patentable if it produces a new result or an old result in a new and more efficient way. This case concerned a quartz mercury vapor tube and the Court found the combination patentable because it supplied a need existing with use of prior art devices. The *Lincoln* case was not cited.

In the second case decided by this Court, *American Steel and Wire Company v. Coe*, 70 App. D. C. 138; 105 F. (2d) 17, claims were drawn to the method of making suspension bridge cables involving the steps of conditioning the cable at the mill and fastening the assembled strands together at the bridge site. The combination was held unpatentable and the Court accepted the theory of the *Lincoln* case.

The "old combination" doctrine and its application to the *Lincoln* case, are discussed in a recent article in *George Washington Law Review*, Volume 11, No. 1, page 90, December, 1942.

It is quite evident that the claims here are not drawn to the same type of "combination" as those which were under consideration in the cases to which reference has been made. There a group of mechanical elements or process steps were claimed and the question arose as to whether such elements

or steps should properly be combined in a patent claim. The claims here are not drawn to such assemblage of elements or steps, but to a unitary dye image which is defined by reference to the components which make it up. The final dye image is neither a developing agent nor a coupler compound, nor can either of these compounds be separately identified in the final dye image. The dye image is just as much a unitary product as though it were claimed by use of a single chemical term or by reference to a chemical formula. This form of claim has been approved by the Supreme Court as pointed out more fully below in the discussion relating to the form of the claims and no question of whether it involves an "old combination" has previously been raised.

The Fischer patent which was cited against the present claims issued in 1914 and the Examiner was able to cite no patents which issued between this date and the date of the present application. The Fischer process was never used commercially and the reason must be apparent from the testimony presented by the plaintiff showing the inoperativeness of certain of the Fischer examples. The Kodachrome method described by the witness Vittum is a commercial process available to the general public today, and the Schinzel examples can be employed as one of the dye images of this commercial material. The Patent Examiner alleges that approximately fifty patents directed to color development have been granted since the issuance of the Fischer patent (Supp. Examiner's Statement, Appellant's App. 67). The truth of this statement is conceded; however, no allegation is made by the Examiner that any of these fifty patents discloses or teaches the present invention, or that if any patent did, it would be early enough to be a reference against the present claims. The Examiner's statement indicates only that there has been recent activity in the field and that, as this Court knows, the desire for natural color photographic pictures has been a long felt need. From 1914 until the filing date of the parent application on which the Schinzel applica-

tion is based, there was no commercial process utilizing the Fischer color method, in spite of the many advantages which such process would possess. Applicant has succeeded in giving this process to the world commercially, and any patentable merit which the dye image possesses should be awarded patent protection. This Court has consistently and recently held that satisfaction of an old and recognized want is highly persuasive of invention (*Levin v. Coe*, ____ Appeals, D. C. ____; 545 O. G. 677).

In discussing the novelty of the dye image claimed, much has been said about the utility of the image in a multi-layer material. However, a multi-layer material containing as the only novel element the dye image of applicant's invention could not have been claimed since it would be an unpatentable combination of elements. The magenta and yellow dye images necessary to a natural color picture would not be a part of the invention, but only the blue-green dye image. Under the "old combination" doctrine, applicant has claimed the blue-green dye image which is the novel feature. While it is intended to be used in a multi-layer material, it is the single patentable element of the material to which claims may properly be drawn.

Form of Claims

The claims here are drawn to a product formed by the chemical coupling of two ingredients. The claim is similar to the following claim which was held valid by the Circuit Court of Appeals for the Sixth Circuit in *Perkins Glue Company v. Holland Furniture Company*, 18 Fed. (2d) 387:

"30. A wood and fiber glue *formed of* a starchy carbohydrate or its equivalent *by union therewith* of about three parts or less by weight of water and alkali metal hydroxide" (italics ours).

In holding this claim valid, the Circuit Court stated that the substantial reference to the claim was to the constituents making up the finished product and was without dependence

on the method by which they were combined. The decision of the Circuit Court was reversed by the Supreme Court in *Holland Furniture Company v. Perkins Glue Company*, 277 U. S. 245, on the ground that the claim did not specify the particular type of starch used, but the form of the claim was approved (page 255).

In the *Perkins Glue* case the claim was drawn to a glue made from two constituents—the starchy carbohydrate and the water solution of an alkali metal hydroxide. The final glue product was neither a starchy carbohydrate nor an alkali metal hydroxide but a new product *formed of* the starchy carbohydrate *by union therewith* of the aqueous solution of alkali metal hydroxide. In the present case the photographic dye image is neither a developing agent nor a coupler compound but a new product *formed by the coupling* of the development product of the developer *with* the coupler compound. The claims under consideration here are drawn, not to an old combination of elements, but to a unitary product having properties not possessed by either of the constituents which go into its production. The claims are drawn in very much the same form as the claim which was approved by the Supreme Court in the *Perkins Glue* case, and are believed to be in the proper form, under the authority of that case.

Claims identical with the claims on appeal here, except for the specific coupler employed, are contained in Mannes, Godowsky and Peterson U. S. patents 2,115,394, granted April 26, 1938, and 2,126,337, granted August 9, 1938. These patents are plaintiff's exhibits 11A and 11B, respectively (Appellant's App. 55 and 57). Claims 10 and 11 of patent 2,115,394 and claims 8, 9, 10 and 11 of patent 2,126,337 are claims similar to the present claims. It will be noted that these patents each contain claims corresponding to the developer claims 1 to 6 of the present application and to the method claims 13 and 14 of the present application.

In referring to the prior Mannes, Godowsky and Peterson patents, we are aware that this Court in cases such as *Fessenden v. Coe*, 69 Appeals D. C. 193, 99 Fed. (2d) 426, has held that claims in an application may be rejected on the prior art notwithstanding that identical claims have been allowed in a prior patent. The facts here, however, are not the same as those in the Fessenden case and similar cases in this Court. The claims presented here are not identical with the claims in the prior patents, but are claims drawn in similar form. The prior patents are cited to show that the form of the claims has been approved by the Patent Office, that the practice has been to accept such claims as being in the proper form, and no adequate reason has been presented by the Commissioner for not allowing claims in the same form in the present case.

Accordingly, we submit that the judgment of the District Court in the instant case should be reversed.

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February 3, 1943.

BRIEF FOR APPELLEE

**In the United States Court of Appeals for the
District of Columbia**

—
APPEAL NO. 8406
—

EASTMAN KODAK COMPANY, APPELLANT

v.

CONWAY P. COE, COMMISSIONER OF PATENTS, APPELLEE

**APPEAL FROM THE JUDGMENT OF THE DISTRICT COURT OF
THE UNITED STATES FOR THE DISTRICT OF COLUMBIA**

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***APPEAL FROM THE JUDGMENT OF THE DISTRICT COURT OF THE
UNITED STATES FOR THE DISTRICT OF COLUMBIA***

BRIEF FOR THE COMMISSIONER OF PATENTS

INTRODUCTION

This is an appeal from the judgment of the District Court of the United States for the District of Columbia (7)¹ dismissing appellant's complaint brought under Section 4915 R. S. (U. S. C. title 35, sec. 63) to authorize the Commissioner of Patents to issue to appellant a patent containing claims 7 to 12, inclusive, of the application of Schinzel, Serial No. 263,945.

¹The number in parenthesis refer to pages in appellant's appendix.

APPELLANT'S APPLICATION

The Schinzel application (27) discloses a method of producing colored photographic images by developing an exposed silver halide emulsion with a primary aromatic amino developing agent in the presence of a coupler compound comprising a naphthol or phenol containing a sulfonamide group.

THE FISCHER PATENT

The patent to Fischer, No. 1,102,028 (62) discloses a method similar to that of Schinzel and employing the same emulsion and developing agent, but a different coupler.

SUMMARY OF ARGUMENT

1. Schinzel's invention is not a new photographic image, but a new coupler compound whose use results in a specifically different dye.

2. The appealed claims are, in effect, drawn to a combination of a dye and a background-forming material. Since this combination is old, the invention, if any, resides in the dye per se rather than in the combination.

3. It being old to produce photographic images by means of dyes, the mere use of a new dye does not produce an inventively new image.

4. The allowance of claims in the Mannes et al., patents, Nos. 2,115,394 and 2,126,337, is not controlling here.

ARGUMENT

The Court below, in its fourth finding of fact (6) held that Schinzel's product differs from that of Fischer

only in the specific coupler compound used and the correctness of this finding does not appear to be disputed by the appellant. This compound has been found to be novel and inventive and has been protected by the allowance of claims 1 to 6, which are found on page 32 of appellant's appendix.

The claims here involved, however, clearly are not limited to the coupler compound, but are drawn to "a photographic image" comprising a dye formed by the coupler compound and a developing agent. A photographic image obviously cannot be formed by dye alone; there must be a contrasting background or material on which the image appears. The claims, therefore, must be construed as calling for the combination of a dye and a background material. It will thus be seen that the claims go two steps beyond the coupler compound, which is the actual invention. They recite this compound as being combined with a developing agent to form a dye, and recite the dye as being arranged to form a photographic image.

The Fischer patent shows it to be old to combine a coupler compound and a developing agent to form a dye, and to use the dye thus produced to form a photographic image. Thus the *combination* here claimed is old. A change in one of the dye-forming ingredients does not produce an inventively different image. The image may, it is true, be improved, but the invention is not in the image itself, but in the particular new ingredient of the dye. It has been old for hundreds of years to combine various ingredients to form paints or dyes, and to use these paints or dyes to form images.

Schinzel did not invent this combination but merely discovered a new ingredient which could be used with advantage.

Schinzel's invention is the coupler compound which is specifically defined in claims 1 to 6 and he should not be permitted to extend his protection to everything which may be in any way improved by the use of this compound. If he is entitled to cover the compound, the dye formed by the use of the compound and an image formed by the use of the dye, it would be equally logical to permit him continue, in the manner of the House that Jack Built, and to claim a picture formed by framing such an image, a room containing such a picture, etc., since it could be argued that the picture and the room were improved as the result of the use of the new compound.

Section 4888 of the Revised Statutes (U. S. C. title 35, sec. 63) provides that an applicant for patent must "particularly point out and distinctly claim the part, improvement or combination which he claims as his invention or discovery." It is thus the clear intent of the statute that the claims shall be limited to the features in which novelty resides, and shall not be extended to cover the association of the new features with old ones in an old way.

In accordance with this statute it has been consistently held that an inventor must limit his claims to the features in which novelty resides and is not entitled to extend them to include old elements which are not inventively combined with the new features. Thus in *Lincoln Engineering Co. of Ill. v. Stewart-Warner Corp.*, 303

U. S. 545, the Supreme Court of the United States said: "The improvement of one part of an old combination gives no right to claim that improvement in combination with other old parts which perform no new function in the combination." The Schinzel coupler compound performs no new function in the combination claimed here. It unites with the developing agent to form a dye, just as other compounds have done, and that dye forms an image in exactly the same manner as other dyes have done. If a better image is formed it is simply because a better dye is used, and not because of any inventive combination between the dye and anything else.

A situation very similar to the present one was presented in *Underwood et al. v. Gerber et al.*, 149 U. S. 224. In that case Underwood had obtained two patents, Nos. 348,072 and 348,073, the former containing a claim to a coloring composition while the latter contained a claim to "a sheet of material or fabric" coated with such composition. The Circuit Court held that the last-mentioned claim was void and that it was the coloring composition itself which was "the only invention which was sufficiently novel to warrant the granting of Letters Patent." In sustaining this ruling, the Supreme Court of the United States said: "There was no patentable novelty or invention, in view of the early patents and publications put in evidence, in applying an existing coloring substance to paper." The situation here differs from that in the Underwood case only in that the claims to the coupler compound are in the same application as the claims to the image, instead of in a separate appli-

cation, but this is immaterial, since the only question involved is whether the image claims define an invention.

Similar holdings of old combination have repeatedly been made by this Court. Thus in *In re McNeil*, 20 App. D. C. 294, it was held that since the combination of a trimmer and stitch forming mechanism was old, the combination of this trimmer with another stitch forming mechanism did not produce a new combination. Similarly, in *In re Ratican*, 36 App. D. C. 95, it was held that, since it was old to use nozzles on street cleaning machines, the use of a new nozzle on such a machine did not result in a new combination. In that case the Court said: "If appellant has made an improvement upon the nozzle of the prior art, he is entitled to be protected in the use of his invention, but he is certainly not entitled to a patent on a new combination merely because he has improved a single element of that combination." Again, in *Krause v. Coe*, 74 App. D. C. 47, it was held that the substitution of one kind of packing for another in a toilet flush valve did not justify a combination claim to such a valve provided with the new packing.

It is urged in the appellant's brief that such cases as those just cited are not pertinent here since the coupler compound loses its identity when mixed with the developing agent and can no longer be identified. This, however, is equally true of the prior coupler compounds, such as that of Fischer. It is not thought that this matter has any bearing on the question as to old combination. Sugar loses its identity, in the ordinary sense

of the word at least, when it is dissolved in coffee, but it could scarcely be contended that a new combination is produced whenever a different kind of sugar is used for this purpose. In this connection attention is directed to *Scientific Tablet Co. et. al. v. Ossege*, 125 F. (2d) 151, affirming 31 F. Sup. 361, in which it was held that the use of flavoring material in tablets, rather than in powdered form, did not produce a patentable combination. Similarly in *In re Ginsburg*, 96 F. (2d) 506, 25 C. C. P. A. 1124, it was held that the substitution of one emulsifier for another in an insecticidal composition did not result in a new combination and in *In re Migrdichian*, 108 F. (2d) 237, 27 C. C. P. A. 806, it was held that a new combination did not result from the substitution of one solvent for another in an insecticide, even though a specifically new composition resulted.

Moreover, even if it is assumed that Schinzel produced a new *dye* which would be patentable per se, the fact remains that the claims are not drawn to a dye per se but to a photographic image formed by this dye. Obviously the dye, in forming the image, acts in the same manner as any other dye, and this was conceded by appellant's witness Vittum (22). Further, it is wholly immaterial, so far as the dye is concerned, whether the image is photographic or whether there is an image at all. The dye might be used for producing solid colors if desired.

In order to justify the allowance of the appealed claims, it would be necessary to find that, even though the specific coupler were old, there would be invention

in using it to form a photographic image. This is clearly not the case since Fischer shows the use of another coupler, in the manner shown by Schinzel, for producing such images. Anyone skilled in the art, who was given the idea of using such a coupler would readily understand that it could be used to produce photographic images, and how it should be used for that purpose.

Schinzel's pictures do not differ inventively from those of the prior art. The improvement resides only in the shade or depth of the colors, and this is a difference in degree only. The improvement of these matters has been the constant aim of inventors ever since color photography began and it would, therefore, not be proper to grant a patent on a picture merely because its coloring was improved. If the appealed claims were allowed the appellant would be able to regulate the sale or use of all pictures formed by the use of their coupler compound, and they might sue, for contributory infringement, anyone who sold film for use with such compound. Clearly, Schinzel's invention does not justify the grant of protection of this scope. He has already been allowed claims which fully protect his new coupler compound. He is no more entitled to claims covering various products which may be made by the use of this compound than the inventor of a new hammer or plane is entitled to claims covering furniture which may be made by its use.

The patents to Mannes et al., appearing on pages 55 to 59 of appellant's appendix, contain claims which are similar in form to those here on appeal. Obviously,

however, the patentability of the present claims is to be determined on its merits. The inadvertent allowance by an examiner, of an unpatentable claim clearly cannot bind the Patent Office or the Courts to allow similar unpatentable claims whenever they are presented. If a mistake has been made in allowing certain claims to Mannes et al., the matter will not be rectified by a similar mistake here. This matter has been repeatedly considered by this Court, and it has been held that the Court will not be controlled by the action taken by the Patent Office in allowing claims in the application on appeal or in other applications (*Dyer v. Coe*, 125 F. (2d) 192; *Minnesota Mining and Manufacturing Co. v. Coe*, 125 F. (2d) 198; *Sharp v. Coe*, 125 F. (2d) 185; *Fessenden v. Coe*, 69 App. D. C. 193, 99 F. (2d) 426). The concurrent decisions of the primary examiner, the Board of Appeals and the District Court in the present case are entitled to far greater weight than the action of a primary examiner in allowing the Mannes et al. patents.

CONCLUSION

It is submitted that the appealed claims are drawn to an old combination involving the union of a developing agent and coupler compound to form a dye and the use of this dye to form a photographic image; that an improvement in the coupler compound does not result in a patentably different dye, and that the use of a new dye does not produce a patentably different photographic image. The claims, therefore, are drawn to an old combination and seek to cover more than Schinzel

has invented. The action of the lower court in refusing the claims was, therefore, proper.

Respectfully submitted.

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